Equilibrium and Non-equilibrium Monte Carlo Simulations of Microphases and Cluster Crystals

by

Kai Zhang

Department of Chemistry
Duke University

Date: ____________________________

Approved:

______________________________
Patrick Charbonneau, Supervisor

______________________________
Stephen Craig

______________________________
Weitao Yang

______________________________
Robert Behringer

Dissertation submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy in the Department of Chemistry in the Graduate School of Duke University 2012
ABSTRACT

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Abstract

Soft matter systems exhibiting spatially modulated patterns on a mesoscale are characterized by many long-lived metastable phases for which relaxation to equilibrium is difficult and a satisfactory thermodynamic description is missing. Current dynamical theories suffer as well, because they mostly rely on an understanding of the underlying equilibrium behavior. This thesis relates the study of two canonical examples of modulated systems: microphase and cluster crystal formers. Microphases are the counterpart to gas-liquid phase separation in systems with competing short-range attractive and long-range repulsive interactions. Periodic lamellae, cylinders, clusters, etc., are thus observed in a wide variety of physical and chemical systems, such as multiblock copolymers, oil-water surfactant mixtures, charged colloidal suspensions, and magnetic materials. Cluster crystals in which each lattice site is occupied by multiple particles are formed in systems with steep soft-core repulsive interactions. Dendrimers have been proposed as a potential experimental realization. In order to access and understand the equilibrium properties of modulated systems, we here develop novel Monte Carlo simulation methods. A thermodynamic integration scheme allows us to calculate the free energy of specific modulated phases, while a $[N]pT$ ensemble simulation approach, in which both particle number and lattice spacing fluctuate, allows us to explore their phase space more efficiently. With these two methods, we solve the equilibrium phase behavior of five schematic modulated-phase-forming spin and particle models, including the axial next-nearest-neighbor
Ising (ANNNI) model, the Ising-Coulomb (IC) model, the square-well linear (SWL) model, the generalized exponential model of index 4 (GEM-4) and the penetrable sphere model (PSM). Interesting new physics ensues. In the ANNNI layered regime, simple phases are not found to play a particularly significant role in the devil’s flowers and interfacial roughening plays at most a small role. With the help of generalized order parameters, the paramagnetic-modulated critical transition of the ANNNI model is also studied. We confirm the XY universality of the paramagnetic-modulated transition and its isotropic nature. With our development of novel free energy minimization schemes, the determination of a first phase diagram of a particle-based microphase former SWL is possible. We identify the low temperature GEM-4 phase diagram to be hybrid between the Gaussian core model (GCM) and the PSM. The system additionally exhibits S-shaped doubly reentrant phase sequences as well as critical isostructural transitions between face-centered cubic (FCC) cluster solids of different integer occupancy. The fluid-solid coexistence in the PSM phase diagram presents a crossover behavior around $T \sim 0.1$, below which the system approaches the hard sphere limit. Studying this regime allows us to correct and reconcile prior DFT and cell theory work around this transition.
To my father
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8.6 First-order FCC2-FCC3 isostructural transition of the GEM-4. Previous thermodynamic integration (TI) results [19] are shown for comparison. $[N]pT$ simulations with histogram reweighting and finite-size scaling estimate $T_c(\infty) = 0.0470(2)$ and $\rho_c(\infty) = 1.2400(3)$. . . . . . . 133

9.1 $[N]pT$ results for the FCC cluster crystal with $N_c = 500$ at $T = 1.5$ and $p = 33.4$. The weights are initialized with the chemical potential $\mu$ at $N_0 = 3910$ (dashed line) and converge to $\tilde{g}_N = 0.00078065N + 9.6940 + 11877/N \langle \circ \rangle$. The constrained Gibbs free energy per particle (solid line), after adding the constant shift $C = 397$, is minimal at $N_{eq} = 3965(10)$. Inset: The converged distribution $P_N$ is flat within the sampled bounds, fluctuating around 1/151 (black line). . . . . . . 136

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E.1 Number of all types of nearest neighbor interactions on the boundary of the cluster before and after spins are flipped. Next nearest neighbor interactions are analogous. Spins in boxes are in the cluster.
List of Abbreviations and Symbols

Symbols

\( \mathbf{r}^N \)   particle position vectors \( \mathbf{r}^N \equiv \{ \mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N \} \)

\( \mathbf{p}^N \)   particle momentum vectors \( \mathbf{p}^N \equiv \{ \mathbf{p}_1, \mathbf{p}_2, \ldots, \mathbf{p}_N \} \)

\( \langle \ldots \rangle \)   ensemble average

\( B \)   bulk modulus

\( D \)   dimension

\( L \)   simulation box size \( V = L^D \)

\( J \)   nearest neighbor ferromagnetic interaction coupling strength in spin models

\( K \)   kinetic energy

\( Q \)   canonical ensemble partition function \( Q(N, V, T) \)

\( Q^{id} \)   relative fluctuation strength in the IC model

\( Q^{id} \equiv \frac{V^N}{N!A^{3N}} \)

\( Z \)   configuration integral \( Z = \int d\mathbf{r}^N e^{-\beta U} \)

\( E \)   energy

\( U \)   potential energy

\( u(r) \)   pair interaction potential of two particles at distance \( r \)

\( V \)   volume

\( \rho \)   particle number density \( \rho = N/V \)

\( F \)   Helmholtz free energy
$f^{id}$ ideal Helmholtz free energy per particle

$G$ Gibbs free energy

$T$ temperature

$p$ pressure

$\mu$ chemical potential

$\mu_c$ chemical potential of lattice sites

$N$ number of particles

$N_c$ number of lattice sites

$n_c$ occupancy, number of particles per lattice site $n_c = \frac{N}{N_c}$

$k$ wavevector with magnitude $k = |k| = 2\pi/\lambda$

$q$ wave number $q = 1/\lambda = k/2\pi$

$\lambda$ wave length

$\alpha$ coefficient of thermal expansion

$\beta$ inverse temperature $\beta = \frac{1}{k_BT}$

$\gamma$ critical exponent of magnetization

$\beta_c$ critical exponent of heat capacity

$\Omega$ number of configurations, density of state

$\Delta$ isothermal-isobaric partition function

$\Xi$ grand canonical partition function

$\Upsilon$ generalized partition function

$\Lambda$ thermal wavelength

$\kappa$ compressibility

$\kappa_c$ relative fluctuation strength in the ANNNI model

$h$ Planck’s constant

$k_B$ Boltzmann’s constant
\( \sigma \) particle hardcore diameter which sets the unit of length scale

\( \epsilon \) depth of attraction well or height of repulsion barrier which sets the unit of energy scale

\( s_i \) spin variable \( s_i = \pm 1 \)

\( g(r) \) radial distribution function

\( \text{erfc}(x) \) error function complementary

**Abbreviations**

ANNNI axial next-nearest-neighbor Ising (called “any”)

BCC body centered cubic

cosex coexistence

CP critical point

ex excess

FCC face centered cubic

GEM-n generalized exponential model of index \( n \)

HS hard sphere

HSF hard sphere under field

IC Ising Coulomb

id ideal gas

LP Lifshitz point

NN nearest-neighbor

NNN next-nearest-neighbor

MC Monte Carlo

MD molecular dynamics

PM paramagnetic-modulated

PSM penetrable sphere model

SALR short-range attraction long-range repulsion
<table>
<thead>
<tr>
<th>Acronym</th>
<th>Description</th>
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<tbody>
<tr>
<td>SC</td>
<td>simple cubic</td>
</tr>
<tr>
<td>SW</td>
<td>square well</td>
</tr>
<tr>
<td>SWL</td>
<td>square well linear</td>
</tr>
<tr>
<td>TI</td>
<td>thermodynamic integration</td>
</tr>
<tr>
<td>3D</td>
<td>three dimensional</td>
</tr>
</tbody>
</table>
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As the nomenclature of the ages of mankind suggests, the evolution of human society
is an epic of materials applications. From stone to metal, from natural minerals to
artificial plastics, the accessibility of materials directly reflects the level of develop-
ment of our civilization. Humans have long cut, milled and shaped materials into a
desired form. But only after we finally understood the mechanism for microscopic
assembly, has it been possible to design materials based on the emergent properties
of its building units. Soft materials are a perfect example of a system where the
nanoscale structures have allowed for such bottom-up self-assembly.

This thesis is concerned about the theory and simulation of soft matter sys-
tems exhibiting spatially modulated patterns on a mesoscale. We will focus on two
canonical examples of this phenomenon: microphase separation and cluster crystals.
Both systems are characterized by many long-lived metastable phases for which the
dynamical relaxation to equilibrium is difficult and a satisfactory thermodynamic de-
scription is missing. Current dynamical theories cannot provide sufficient guidance
because understanding the thermodynamics is the prerequisite. We will show how
computer simulations help us solve the equilibrium properties of certain modulated-
phase-forming models in the following chapters. This first chapter introduces both microphases and cluster crystals, as well as their physical foundations.

1.1 Microphase Separation

Spatially modulated phases containing lamellae, cylinders, clusters, etc., in which periodic domains are separated on the mesoscopic scale, are observed in a wide variety of physical and chemical systems [24]. These *microphases*, such as multiblock copolymers [25–29], oil-water surfactant mixtures [30], charged colloidal suspensions [31–33], and magnetic materials [34], are of particular industrial and academic interest, because of their special mechanical and structural properties. As one of the most extensively studied and technologically developed soft matter systems, block copolymers are used for instance as thermoplastic elastomers [29] because their various microphases can be crosslinked and are easily molded, and as templates for nanosstructure fabrication [35, 36] because of the nanometer scale of their patterns. Microphase formation has also been hypothesized to play a role in biological membrane organization [37] and in the formation of stripes in certain superconductors [38–43], although the microscopic interpretation is still debated. These self-assembled microphase patterns typically result from the competition between short-range attractive and long-range repulsive (SALR) interactions. The nature of these interactions varies greatly from one system to the next, as shown in Table 1.1, but the phenomenology is universal. Insights gained from the study of one system therefore commonly translate to the study of another.

Simple van der Waals-like liquids, with only hard-core repulsion and isotropic attraction, such as depletion attraction in colloids, show liquid-gas phase separation at low temperatures and intermediate density (see FIG. 1.1a and 1.1b). In contrast, for frustrated potentials, where long-range repulsion is also present, modulated phases are thermodynamically more favorable than the completely separated gas and liq-
Table 1.1: Examples of systems exhibiting microphases and the nature of the competing interactions

<table>
<thead>
<tr>
<th>System</th>
<th>Source of competition</th>
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<tbody>
<tr>
<td>Magnetic materials</td>
<td>Ferromagnetic vs. antiferromagnetic spin coupling</td>
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<tr>
<td>Diblock copolymers</td>
<td>Covalent bond vs. immiscibility monomers</td>
</tr>
<tr>
<td>Oil-water micellar solution</td>
<td>Hydrophobic vs. hydrophilic interactions</td>
</tr>
<tr>
<td>Colloidal suspensions</td>
<td>Depletion attraction vs. screened Coulomb repulsion</td>
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uid phases under the same condition (see FIG. 1.1c and 1.1d). Below a certain temperature, the point at which the entropic penalty of forming microphases is less important than its energetic stabilization, the modulated texture is thermodynamically stable. At high temperatures entropy dominates, so the microphases give way to a supercritical-fluid-like disordered phase. The order-disorder phase transition between the two regimes, which is generally second order at the critical point for purely attractive potentials, can become (weakly) first order when the frustration is sufficiently strong [44]. The frustration strength is indeed an important factor in the formation of modulated phases. Generally, microphase separation occurs only when the frustration is large enough to break up the gas and liquid phases into microphase patterns. This repulsion threshold defines the triple point where the ordered, disordered and modulated phases meet on a $T$–frustration phase diagram (FIG. 1.2). If more than one of the three transitions, namely the order-disorder, the modulated-disorder and the order-modulated transitions, are of second order, the triple point is a multicritical point called the Lifshitz point (LP)$^1$ [47].

Although the modulated organization is spontaneous, obtaining detailed morphological control is notoriously difficult. Annealing [48], external fields [49], strain compression [50], or complex chemical environments [51–53] are often necessary to order diblock copolymers, for instance. Understanding how to tune and stabilize

$^1$ In the literature [45, 46], the frustration threshold, beyond which the vapor-liquid transition is replaced by the vapor-modulated transition, is sometimes called the Lifshitz point, even though the second transition is fluctuation-induced first order rather than second order.
microphases is essential to broadening their material relevance for self-assembly, yet experimental systems provide limited microscopic insights. A number of schematic continuous space [32, 33, 45, 54–57] and lattice [6, 28, 58–64] models have been devised to obtain more microscopic insights from theory and simulations. Some of these models have even become textbook material [65, 66]. Grasping their equilibrium properties is necessary to resolve problems surrounding the non-equilibrium assembly of microphases [67–69]. But although the modulated regime is a key feature of these models, it has not been accurately characterized in any of them. Even

Figure 1.1: (a) Simple isotropic liquid potential. (b) The schematic $\rho$–$T$ phase diagram of (a). In the coexistence phase region the system separates into a vapor of density $\rho_v$ and a liquid of density $\rho_l$. (c) Frustrated potential. (d) The schematic $\rho$–$T$ phase diagram of potential model (c). In the modulated phase region the system exhibits separated domains on a mesoscopic scale.
for the most schematic versions, existing theoretical treatments have only offered limited assistance.

Direct computer simulations have also been unable to provide reliable equilibrium information \([66, 70]\). Traditional simulation “tricks” for facilitating ergodic sampling of phase space by passing over free energy barriers, notably parallel tempering and cluster moves, are of limited help in microphase-forming systems. Because of the dependence of the equilibrium periodicity on temperature, sampling higher temperatures leaves the system in a modulated phase with the wrong periodicity; and because of the lack of simple structural rearrangements for sampling different modulations, the efficiency of cluster moves is limited. In this thesis, we overcome this hurdle by developing a free-energy integration method and applying it to two Ising spin-based and one particle microphase-forming models.

1.2 Cluster Crystal

Motivated by the ubiquity of repulsive electromagnetic interactions, most models for matter include a core component that diverges at zero separation, which results
in a first-order fluid-crystal (or order-disorder) transition. Except for a few exotic examples, such as certain bosonic systems [71, 72], simple fluids of atoms and small molecules thus similarly crystallize. Yet when nano- and micro-scale particles are concerned, more complex models that include bounded repulsive interactions are also conceivable. Soft and mostly empty particles, such as dendrimers, can sit on top of each other with only a finite energy penalty [73] (Fig. 1.3). A soft-core interaction captures the effective coarse-grained nature of the potential of mean force between them [74], and at relatively low densities these interactions are reasonably pairwise additive [75].

Liquid state theory suggests that the phase behavior of such soft-core repulsive interactions falls into one of two categories, depending on the presence or not of negative components in the Fourier transform of the pair potential – or, roughly speaking, on its steepness [76, 77]. On the one hand, flat potentials with purely positive Fourier transforms undergo reentrant melting. Under compression at low temperatures, the system first crystallizes and then remelts (Fig. 1.4 and Fig. 1.5). The Gaussian core model (GCM), which was first proposed as a model for plastic crystals [78] and has since been thoroughly studied [79–82], exhibits such behavior. On the other hand, steep potentials with negative Fourier components cluster up at
Figure 1.4: Soft-core potential (solid lines) generated by particles on a periodic lattice (filled circles) and the overall potential (dashed line) felt by sample test particles (empty circles). Left: GEM-2 (GCM) produces an overall flat potential and exhibits reentrant melting. Right: GEM-4 produces potential barriers between lattice sites which results in clustering.

Figure 1.5: Schematic temperature-density phase diagrams of the GCM exhibiting reentrant melting (left) and of the GME-4 exhibiting clustering (right).

high densities. Under compression, these systems form crystals in which each lattice site may be occupied by multiple particles (Fig. 1.4 and Fig. 1.3). The transition from fluid to cluster crystals is driven not only by gains in free volume, but also by reductions of the overlap energy \[77\]. The penetrable sphere model (PSM) belongs to this second category \[83\]. To complement these two systems, Mladek et al. have introduced the generalized exponential model of index \(n\) (GEM-\(n\)), with a pair potential that scales with distance \(r\) like \(\exp(-r^n)\), to interpolate between the GCM
Like for microphase formers, studying the thermodynamics of cluster crystals by simulations is particularly challenging. When initializing the system, there is a trade-off between configurations with more lattice sites but fewer overlaps, and configurations with fewer lattice sites but more overlaps. The problem is that once initialized, (reasonably) finite systems cannot find the average lattice site occupancy $n_c^{eq}$ because no simple ensemble allows for the lattice spacing and occupancy to simultaneously relax [15, 77, 85]. Incommensurability and high free energy barriers to reorganization get in the way. A free energy scheme based on an extended thermodynamic description is therefore necessary to locate the equilibrium phase. In this thesis, we solve the equilibrium properties of two cluster-crystal-forming models, the GEM-4 and the PSM, using thermodynamic integration and the $[N]pT$ ensemble method that we develop and refine.
To effectively describe the collective behaviors of many-body systems, on-lattice spin or off-lattice particle models are often constructed. A good physical model is coarse-grained and omits irrelevant microscopic details on smaller scales, but is still able to capture the physics occurring on the scale of interest.

Lattice models strip away the complexity due to packing and help reveal the influence of nongeometrical factors. The Ising model, for instance, offers a singular window on critical phenomena and on gas-liquid coexistence; Flory-Huggins’s theory of solvated polymers is core to the physics of polymers; and spin glasses are key sources of inspiration for the difficult problem of structural glass formation. If a lattice model of a system exists, it is often a good strategy to solve it before embarking on a study of more elaborate variants. Microphase formation is one such phenomenon that could benefit from further consideration of lattice-based models.

In general, a two-state spin system with spin variable $s_i = \pm 1$ is defined by a Hamiltonian

$$ H = J_0 + J_1 \sum_i s_i + J_2 \sum_{i,j} s_i s_j + J_3 \sum_{i,j,k} s_i s_j s_k + \cdots, \quad (2.1) $$
where $J_n$ is the coupling constant between $n$ interacting spins. For instance, a ferromagnetic Ising model has $J_n = 0$ for all $n \geq 3$ and pairwise interactions with coupling $J_2 < 0$ between nearest neighbors $\langle i, j \rangle$.

Although a lattice model is somewhat easier to solve, it introduces an artificial geometry to the system that prevents the consideration of packing structures in solids. In addition, problems related to pressure cannot be studied on a filled lattice because there is no $pV$ work. Due to these limitations, an off-lattice particle model is often needed. Hard spheres (HS) are a canonical particle model whose study successfully predicted a crystallization transition in colloidal systems. The FCC crystals they form at high densities are a natural consequence of effective packing of the space under volume exclusion.

In continuous space, the Hamiltonian of a system with $N$ particles of mass $m$ that sit at position vectors $\mathbf{r}^N \equiv \{ \mathbf{r}_1, \mathbf{r}_2, ..., \mathbf{r}_N \}$ and move with momenta $\mathbf{p}^N \equiv \{ \mathbf{p}_1, \mathbf{p}_2, ..., \mathbf{p}_N \}$, is generally written as

$$H(\mathbf{r}^N, \mathbf{p}^N) = K(\mathbf{p}^N) + U(\mathbf{r}^N) = \sum_{i=1}^{N} \frac{p_i^2}{2m} + U,$$  \hspace{1cm} (2.2)

where the kinetic energy $K(\mathbf{p}^N)$ is configuration-independent and the potential energy $U(\mathbf{r}^N)$ usually assumes a pairwise additive form

$$U(\mathbf{r}^N) = \sum_{i>j} u(r_{ij}).$$  \hspace{1cm} (2.3)

In the rest of this work, we only consider the two-body interactions $u(r_{ij})$ between isotropic particles $i$ and $j$, although many-body effects and anisotropic interactions may also play important roles in certain systems.

In the sections that follow, we first introduce two spin (ANNNI and IC) and one particle (SWL) models that can form microphases. We will then discuss the cluster crystal forming models, the PSM and the GEM-$n$.  

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2.1 Notations of Lamellar Phases on Lattice

Before introducing the models, a clarification of the nomenclature for describing layered microphases on a lattice is in order. This nomenclature does not directly translate in a continuous space context, but the analogy will be useful there as well. Two conventions for characterizing the periodicity of lamellar phases coexist in the scientific literature. The first notation compactly identifies a phase with a simple wave number \( q = 1/\lambda \) (in units of \( 2\pi \)), where \( \lambda \) is the period length. The second, a short-hand form \( \langle m^j n^k \rangle \) introduced in Ref. [5], is less compact but provides a more intuitive description of the layered phase. In this notation, integers are used to describe a lamellar phase formed by periodic repetition of patterns of \( j \) pairs of opposite-spin lamellae of width \( m \) followed by \( k \) pairs of opposite-spin lamellae of width \( n \) (Fig. 2.1). For example, phase \( \langle \infty \rangle \) is the ferromagnetic phase and phase \( \langle 2 \rangle \) consists of two layers of spins up followed by two layers of spins down. But phase \( \langle 23 \rangle \) has a period \( \lambda = 5 \), because thermal fluctuations blur the layer boundaries and the thickness of each lamella takes the average value

\[
\frac{\lambda}{2} = \frac{mj + nk}{j + k}.
\]  

(2.4)

This notation, which can only represent phases of rational periodicity, is well suited for the commensurate phases that are observed on a lattice with periodic boundary conditions.

2.2 Axial Next-Nearest-Neighbor Ising (ANNNI) Model

The ANNNI model was first introduced to rationalize helical magnetic order in certain heavy rare-earth metals [59–61, 86]. The simple model’s description of the experimentally observed order is only qualitative [87], but because of its surprisingly complex phase behavior, it is now canonical for the study of systems with competing
interactions [65, 66]. Its Hamiltonian on a simple cubic lattice

\[ H_{\text{ANNNI}} = -J \sum_{\langle i,j \rangle} s_is_j + \kappa J \sum_{[i,j]_z} s_is_j \tag{2.5} \]

is expressed for spin variables \( s_i = \pm 1 \) coupled through a positive constant \( J \). With the Boltzmann constant \( k_B \), \( J/k_B \) sets the temperature \( T \) scale. Alignment is favored for nearest-neighbor pairs \( \langle i,j \rangle \), but frustrated with relative strength \( \kappa > 0 \) for \( z \)-axial next-nearest-neighbor pairs \( [i,j]_z \). The exact solution of the one-dimensional version of the model provides \( T = 0 \) phase information for all other dimensions [5]: ferromagnetic order is the ground state for \( \kappa < 1/2 \), while the layered antiphase \( \langle 2 \rangle \) minimizes the energy for \( \kappa > 1/2 \). A mean-field description qualitatively captures the higher-dimensional, finite-\( T \) features of the model [13, 88]: the system is paramagnetic at high \( T \); it is ferromagnetic at low \( T \) and \( \kappa \); and modulated layered phases form for sufficiently high \( \kappa \) [61]. These three regimes join together at a multicritical Lifshitz point \( (\kappa_L, T_L) \) whose special critical properties have been pre-
dicted by theory [47, 89, 90] and verified in simulations [2, 91]. High-temperature series expansions have also been used to study the paramagnetic phase and predict its limit of stability [3, 10]. These predictions were confirmed by finite-size critical rescaling for the paramagnetic-ferromagnetic (PF) transition [1, 5, 92, 93] and by heat capacity [4, 5] and generalized susceptibility [94] measurements for the paramagnetic-modulated (PM) transition. For $\kappa < \kappa_L$, the PF transition has Ising universality [1, 95]; while for $\kappa > \kappa_L$, the PM transition has been argued to have XY universality [8, 9, 59], but direct simulation verifications are incomplete [94] and the results of the high-temperature series expansion analysis are inconclusive [3, 96]. The ferromagnetic-modulated (FM) transition is predicted by a Landau-Ginzburg treatment to be first order with $q$ changing discontinuously from 0, and to be tangent to the PF and PM transition lines at the Lifshitz point [97].

Commensurate $\langle 2^3 j^3 \rangle$ phases spring from the multiphase point at $T = 0$ and $\kappa = 1/2$. The structure of the branching processes at low $T$ has been carefully studied [98], and forms the basis for the low-temperature series expansion [11]. For the rest of the modulated regime, approximate theoretical treatments, such as a mean-field theory with a soliton correction [99], an effective-field theory [100], and the tensor product variational approach (TPVA) [12] have been used. Monte Carlo simulations have also been carried out in this regime [5, 93], but the hysteresis resulting from the high free-energy barriers that separate modulated phases from each other limits accurate determinations of the phase boundaries from annealing-based approaches [60, 94]. Avoiding annealing is thus preferable for accurately locating transitions within the modulated regime [94]. It is thought that incommensurate phases and interfacial roughening can lower the transition free energy barriers between different commensurate modulated phases on sufficiently large lattices [98], but these phases have not been observed thus far.
2.3 Ising-Coulomb (IC) Model

The Ising-Coulomb (IC) model, in which the nearest neighbor ferromagnetic coupling spin is frustrated by long-range Coulomb interaction of relative strength $Q$, was first suggested as a model for the stripe phase behavior of high-temperature superconductors in two dimensions [64, 101]. It was also adopted as a generic coarse-grained description of microphase formation in systems with competing pair interactions in three dimensions [6, 7, 102], and used to study the effect of dispersion forces on phase transitions in ionic systems [103]. Although it is based on the Ising model, its Hamiltonian

$$H_{\text{IC}} = -J \sum_{\langle i,j \rangle} s_i s_j + QJ \sum_{i>j} \frac{s_i s_j}{r_{ij}}, \quad (2.6)$$

does not allow ferromagnetic ordering for any $Q > 0$, i.e., an infinitesimally small Coulomb frustration is sufficient to induce layering at low $T$ [102]. By analogy with a Landau-Ginzburg model with frustration [64, 101, 104, 105], it is, however, expected that any screening of the Coulomb interaction moves the onset of modulation to a finite $Q$ [106, 107]. Note that the $Q \to \infty$ limit recovers the simple-cubic lattice restricted primitive model (LRPM) of Dickman and Stell at full occupancy [108, 109].

The one-dimensional $T = 0$ phase sequence is known to be made of equal length blocks of alternating orientation [110]. In higher dimensions, although no rigorous demonstration exists, layered phases of integer periodicity are also expected to be the ground state at low $Q$ [7]. In that regime, an approximate mapping to a one-dimensional system seems reasonable. For sufficiently large $Q$, two- and three-dimensional periodic structures, i.e., “cylinders” and “clusters”, minimize the energy; and for $Q > Q_N^0 \approx 15.33$ antiferromagnetic Néel order is expected [7]. Mean-field treatments [7, 103] and Monte Carlo simulations (for $Q < 1$) [6] describe the paramagnetic-modulated (PM) transition. Although the mean-field treatment over-
estimates the transition temperature [7, 103], its predictions are nonetheless quite similar to the phase behavior obtained from simulations [6]. Because of the long-range isotropic Coulomb interaction, the transition is “fluctuation-induced” first order for any \(0 < Q < Q_N\) [44, 111], and at low \(Q\) the modulated phases melt at \(T_c(Q) \sim T_c(0) - Q^{1/4}\), where \(T_c(0) \approx 4.51\) is the 3D Ising simple cubic critical point [102]. For \(Q \geq Q_N\) the continuous paramagnetic-Néel (PN) transition has Ising universality, and at high \(Q\), the critical temperature \(T_c(Q) \sim T_c(\infty)Q - T_c(0)\) [7], where the trivial linear dependence results from the choice of units and \(T_c(\infty) \approx 0.515\) is the LRPM result [108, 112]. A triple point connects the paramagnetic, modulated cluster, and antiferromagnetic Néel phases at \((Q_N, T_c(Q_N))\), but only the mean-field estimates for the transition location \(Q_N = 36/\pi \approx 11.5\) and \(T_c(Q_N) = 1.61\) are known [7]. Within the modulated layered regime proper, phases spring out at the boundary between neighboring low-temperature ground states of integer periodicity [6]. The process is akin to that observed between the antiphase and the ferromagnetic phase in the ANNNI model. The simulations in the layered regime capture the presence of these phases, but the use of a simulated-annealing approach in a strongly hysteretic regime is likely to bias the estimates for the transition temperatures [6].

2.4 Square Well Linear (SWL) Model

To study microphases in continuous space, we use a SALR potential of the form

\[
u(r) = \begin{cases} 
\infty, & r < \sigma \\
-\epsilon, & \sigma < r < \lambda \sigma \\
\xi \epsilon (\kappa - r/\sigma), & \lambda \sigma < r < \kappa \sigma \\
0, & r > \kappa \sigma 
\end{cases}
\]  

(2.7)

with hardcore diameter \(\sigma\), attraction range \(\lambda \sigma\), repulsion range \(\kappa \sigma\) and repulsion strength \(\xi \epsilon > 0\) (Fig. 2.2). Adding a linear repulsion to the square-well (SW) attrac-
Figure 2.2: The interaction potential of SWL with $\lambda = 1.5$, $\kappa = 4$ and $\xi = 0.2$.

...tion results in a square-well linear (SWL) form. Because the hard core diameter is clearly defined and the repulsion range is finite, it is a computationally convenient model to study SALR, although it does not have direct experimental equivalent.

If the repulsion is sufficiently strong, namely if $\xi$ brings the system beyond a threshold, and of the appropriate range, we expect the SWL model to form various microphases such as lamellae(L), cylinders (C), gyroid (G), and spherical clusters (S) of FCC or BCC symmetry by analogy with the mean-field behavior of model diblock copolymers [113].

2.5 Penetrable Sphere Model (PSM) and Generalized Exponential Model of Index $n$ (GEM-$n$)

The penetrable sphere model (PSM) was first introduced by Marquest and Witten as a prototype for soft matter interactions [83], and shows a behavior analogous to that of the microphase-forming systems. It is described by a pair potential

$$ u(r) = \begin{cases} 
\epsilon & \text{for } 0 \leq r \leq \sigma \\
0 & \text{for } r > \sigma, 
\end{cases} $$

(2.8)
where $\sigma$ is the soft core diameter and $\epsilon > 0$ is the repulsion barrier height. The vocabulary “penetrable sphere model” is also confusingly used for the Widom-Rowlinson (WR) model, in which overlapping particles attract with many-body interactions determined by the total occupied volume [114, 115]. The WR model, however, thermodynamically maps into a binary mixture with non-additive hard-core repulsions [116], not to the model studied here.

The PSM can be related to the generalized exponential model of index $n$ (GEM-$n$) [84], with pair potential

$$u(r) = \epsilon e^{-(r/\sigma)^n},$$

which changes from the $n = 2$ Gaussian core model (GCM) to the $n \to \infty$ PSM limit (Fig. 2.3). Based on liquid state theory arguments, one expects that systems with bounded yet harshly repulsive pair interactions, such as the GEM-$n$ with $n > 2$ [76, 84], should form face-centered cubic (FCC) cluster crystals at high $T$ and number density $\rho \equiv N/V$. The $N_c$ lattice sites then have an average occupancy $n_c = N/N_c \geq 1$.

The phase behavior of the PSM has not been accurately determined, but some of its general features are reasonably well understood. Density functional theory (DFT) predicts that $n_c$ increases linearly with $\rho$ at high $T$ [22, 76], while at low $T$ the fluid-solid transition approaches the hard sphere limit [21]. A cell theory treatment further suggests that increasing $\rho$ in the low $T$ regime results in a continuous evolution of the lattice occupancy [20, 21].

The high-temperature equilibrium phase diagram of the GEM-4 was first studied by DFT [84] and lattice Monte Carlo simulations [15, 77]. In addition to FCC cluster crystals, a body-centered cubic (BCC) phase was found to be the first solid to form upon compression. Phonon theory [17, 117] and simulations [19] have predicted a series of first-order isostructural transitions and critical points, in contrast to the
Figure 2.3: The interaction potential of GEM-\(n\) for \(n = 2, 4, \infty\), where GEM-2 is equivalent to GCM and GEM-\(\infty\) is equivalent to PSM.

Continuous changing of \(n_c\) in the PSM, but this behavior has not been completed in simulations.
Thermodynamics and Statistical Mechanics

In this chapter, we first review some basic conceptions in thermodynamics and statistical mechanics, which allows us to introduce more clearly the expanded thermodynamics of cluster crystals and the \([N]pT\) ensemble in Chapter 5.

3.1 Thermodynamics

Thermodynamics dates back to the 19th century when heat engines started playing a key role in the industrial revolution. A phenomenological theory, thermodynamics is mainly concerned about the relations between macroscopic thermal quantities, such as energy, heat, work, temperature and pressure, making abstractions of the underlying microscopic mechanisms. In thermodynamics, deviations of thermal quantities from their mean values, i.e., fluctuations, are neglected other than as conditions for stability. Although the macroscopic systems concerned in thermodynamics are treated like black boxes, logical deductions and careful experimentations in a context of positivism established a paradigm for scientific discovery, making this science not only survive but also thrive the advent of atomic physics and quantum mechanics [118]. To this day, thermodynamics still provides the most robust theoretical
framework for analyzing the equilibrium properties of thermal systems.

While the dynamical state of a $N$ particle system is specified by $6N$ positions and velocities, a thermodynamical state is characterized by only a few macroscopic variables, which can be either intensive, such as temperature $T$ and pressure $p$, or extensive, such as volume $V$ [119]. A system is in a steady state when its properties do not vary over a macroscopic timescale, as long as the external conditions remain unchanged. A steady state subject to mechanical, chemical and thermal equilibrium, is a thermodynamic equilibrium (stable or metastable) state. Functions that depend only on the state, thus on a few constraint parameters, such as internal energy $E$, entropy $S$, enthalpy $H$, Helmholtz free energy $F$ and Gibbs free energy $G$, are called state functions and the free energies are sometimes referred to as thermodynamic potentials, in analogy to energetic interactions. When the system is in a state, or subject to certain external constraints, it still visits different dynamical states over time as a result of molecular motion. Only when a given collection of dynamical states are visited at the right frequency is the system at equilibrium and the thermodynamic potentials are optimized.

Given a set of external parameters, there exists a state function that has these parameters as natural variables. Different state functions are related by Legendre transformations when the external parameters are changed [120]. We list some of the ones most commonly used in Table 3.1. The state functions with the constraints as natural variables are expressed in full differential form, from which we can get some basic thermodynamic relations, for instance,

$$p = -\left(\frac{\partial F}{\partial V}\right)_T.$$  

(3.1)

A thermodynamic phase is a homogeneous mixture of chemical constituents that has a definite boundary. It is well known that normal pure substances can stay in one
Table 3.1: Thermodynamic state functions and their full differential forms with respect to corresponding natural variables.

<table>
<thead>
<tr>
<th>Constraints</th>
<th>State function</th>
<th>Differential form</th>
</tr>
</thead>
<tbody>
<tr>
<td>NVE</td>
<td>S</td>
<td>( TdS = dE + pdV - \mu dN )</td>
</tr>
<tr>
<td>NVS</td>
<td>E</td>
<td>( dE = TdS - pdV + \mu dN )</td>
</tr>
<tr>
<td>NpS</td>
<td>H = E + pV</td>
<td>( dH = TdS + Vdp + \mu dN )</td>
</tr>
<tr>
<td>NVT</td>
<td>F = E - TS</td>
<td>( dF = -SdT - pdV + \mu dN )</td>
</tr>
<tr>
<td>NpT</td>
<td>G = H - TS</td>
<td>( dG = -SdT + Vdp + \mu dN )</td>
</tr>
</tbody>
</table>

of the three common phases: gas, liquid and solid. Given the phase of a substance, the number of thermodynamic variables (\( T, p, \mu, \) etc.) that can be freely changed are subject to the Gibbs’ phase rule

\[
f = 2 + \nu - \phi,
\]

where \( f \) is the number of degrees of freedom, \( \nu \) is the number of independent chemical components and \( \phi \) is the number of phases. For instance, pure liquid water has \( f = 2 \) corresponding to arbitrary pairs of \( T \) and \( p \) with the third intensive variable \( \mu(T,p) \) implicitly depending on them. At liquid-gas coexistence, \( f = 1 \) which means that for each coexisting \( T_{\text{coex}} \), there is only one \( p_{\text{coex}} \) (or \( \mu_{\text{coex}} \)).

3.1.1 Thermodynamics of Cluster Crystals

Inspired by the generalized thermodynamics of systems with vacancies and interstitials [85], phase rules that take into account the possibility that crystals have multiple particles occupying each lattice site have been formulated [15, 77]. In order to specify an equilibrium phase, Mladek et al. introduced an additional pair of thermodynamic variables: the number of lattice sites \( N_c \) and an associated chemical potential-like quantity \( \mu_c \), roughly corresponding to the free energy penalty of inserting a lattice site. In this expanded formulation, the constrained Helmholtz free
energy $F_c(N,V,T,N_c)$ has an exact differential form

$$dF_c = -SdT - pdV + \mu dN + \mu_c dN_c,$$

where $\mu$, $p$, and $S$ are all implicit functions of $n_c$, and at equilibrium $F(N,V,T) = F_c(N,V,T,N_c^{eq})$. The constrained Gibbs free energy $G_c(N,p,T,N_c) = \mu N + \mu_c N_c$ has a similar differential form

$$dG_c = -SdT + V dp + \mu dN + \mu_c dN_c,$$

and $G(N,p,T) = G_c(N,p,T,N_c^{eq})$. Because $\mu$ and $\mu_c$ are functions of $N_c$, they do not correspond to the system’s equilibrium quantities unless $N_c$ minimizes the overall free energy of the system, i.e.,

$$\left( \frac{\partial F_c}{\partial N_c} \right)_{N,V,T;N_c=N_c^{eq}} = 0; \quad (3.5)$$

or

$$\left( \frac{\partial G_c}{\partial N_c} \right)_{N,p,T;N_c=N_c^{eq}} = 0. \quad (3.6)$$

Equilibrium thus occurs when the driving force for changing the number lattice sites vanishes, i.e., $\mu_c = 0$.

It is computationally much more convenient to fix $N_c$ and vary $N$ than to change $N_c$ at fixed $N$. The free energy minimization is thus applied on per-particle quantities

$$f_c(\rho,T,n_c) \equiv \frac{F_c(N,V,T,N_c)}{N} = \mu + \frac{\mu_c}{n_c} - pv$$

$$g_c(p,T,n_c) \equiv \frac{G_c(N,p,T,N_c)}{N} = \mu + \frac{\mu_c}{n_c},$$

where $v = 1/\rho$. The corresponding differential forms, which simplify to the standard expressions when $\mu_c = 0$,

$$df_c = -sdT - pdv - \frac{\mu_c}{n_c^2} dn_c$$

$$dg_c = -sdT + vdp - \frac{\mu_c}{n_c^2} dn_c.$$
Figure 3.1: Schematic illustration of $\frac{\partial Y(x,N_{eq}^c(x))}{\partial x}$. Fixing the other parameters, the thermal quantity $Y$ is a function of $x$ and $N_c$ illustrated by the surface $ABCD$, but only $AC$ is an equilibrium curve (red). In an infinitesimal volume, the surface $ABCD$ is a plane. The total derivative $\frac{\partial Y(x,N_{eq}^c(x))}{\partial x}$ is taken along $AC$, which projects onto the curve $N_{eq}^c(x)$ ($A'C$). As $x$ changes by $dx$ ($A'B'$), the equilibrium $Y$ changes from point $A$ to point $C$ by the amount represented by $AA'$, and therefore, $\frac{\partial Y(x,N_{eq}^c(x))}{\partial x} = \frac{AA'}{A'B'}$. Because $AA' = AM + MA'$, the equilibrium derivative can be divided into two parts. The first part equals $\frac{AM}{A'B'} = \frac{AM}{MB} = (\frac{\partial Y}{\partial x})_{N_{eq}^c}$, while the second part equals $\frac{MA'}{A'B'} = \frac{BB'}{A'B'} = \frac{BB'}{BC} \frac{B'C}{A'B'} = \lim_{A'B' \to 0} \frac{AN}{ND} \frac{B'C}{A'B'} = \left(\frac{\partial Y}{\partial N_c}\right)_x \left(\frac{\partial N_{eq}^c}{\partial x}\right).

are obtained using the generalized Gibbs-Duhem relation

$$Nd\mu + N_c d\mu_c = -SdT + Vdp,$$

and provide the minimization conditions

$$\left(\frac{\partial f_c}{\partial n_c}\right)_{p,T;n_c=n_{eq}^c} = 0$$  \hspace{1cm} (3.8)

$$\left(\frac{\partial g_c}{\partial n_c}\right)_{p,T;n_c=n_{eq}^c} = 0.$$  \hspace{1cm} (3.9)

This thermodynamic construction provides important physical insights into the equilibrium response functions of cluster crystals. The heat capacity $C_V$, bulk modulus (or compressibility) $B(\equiv \kappa^{-1})$ and coefficient of thermal expansion $\alpha$, for instance,
can be described as having two separate physical contributions. The first comes from “normal” crystal relaxation, i.e., an affine transformation under compression, and the second from clustering. For reasons that will become clearer below, the affine component is also dubbed the virial contribution.

The response function is generally defined as the derivative of a thermal quantity $Y$ (energy, enthalpy, volume, etc.) with respect to a changing parameter $x$ (temperature, pressure, chemical potential, etc.). In cluster crystals, $Y$ itself is a function of $N_c^{eq}$, which in turn depends on $x$, so

$$\frac{\partial Y(x, N_c^{eq}(x))}{\partial x} = \left( \frac{\partial Y}{\partial x} \right)_{N_c=N_c^{eq}} + \left( \frac{\partial Y}{\partial N_c} \right)_{x; N_c=N_c^{eq}} \left( \frac{\partial N_c^{eq}}{\partial x} \right),$$

where the two terms correspond to the virial and clustering mechanisms, respectively (Fig. 3.1). The differential can be obtained for any $n_c$, but only has a clear-cut thermodynamic interpretation when its value is calculated for the equilibrium cluster occupancy. The bulk modulus of cluster crystals, for instance,

$$B \equiv -V \left( \frac{\partial p(N, V, T, N_c^{eq})}{\partial V} \right)_{N,T},$$

has an additional softening contribution due to clustering. Under compression, the lattice relaxes not only by affinely reducing the lattice constant, but also by eliminating lattice sites and clustering [15, 19, 77]. Analogously, the expression for the coefficient of thermal expansion

$$\alpha \equiv \frac{1}{V} \left( \frac{\partial V(N, p, T, N_c^{eq})}{\partial T} \right)_{N,p},$$

$$= \frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_{N_c=N_c^{eq}} + \frac{1}{V} \left( \frac{\partial V}{\partial N_c} \right)_{N_c=N_c^{eq}} \left( \frac{\partial N_c^{eq}}{\partial T} \right)_{N,p}$$

(3.11)
reveals that under isobaric heating, the expansion of the lattice to produce more free volume for each cluster is accompanied by breaking up the clusters themselves. The decrease of $n_{eq}^c$ with $T$ requires additional volume.

Instead of calculating the thermal derivative, response functions can also be expressed as fluctuations of thermal quantities, e.g., $C_V = \beta(\langle E^2 \rangle - \langle E \rangle^2)/T$ [121, 122]. Although formally also true for cluster crystals, special attention needs to be given to $N_c$ being held fixed in simulations. In that case, the calculated fluctuations only capture the affine contribution from the lattice. In other words, the simulation at fixed $N_c$ does not measure the fluctuation of equilibrium lattices, but of lattices constrained to the specific equilibrium occupancy at one phase point. The clustering contribution must thus be separately calculated, in order to capture the correct equilibrium behavior.

3.2 Statistical Ensembles

Statistical mechanics is the probability theory of a large number of particles, or more generally, of a large number of degrees of freedom. A statistical ensemble is a collection of configurations (microstates) of the system subject to certain constraints. A configuration in ensemble theory corresponds to a dynamical state alluded to in the discussion of thermodynamics. While the thermodynamic value $\langle A \rangle$ of a physical quantity $A$ is the time average along the system’s trajectory through phase space, it is equivalent to the weighted average over all configurations in the ensemble, if ergodicity is satisfied [123]. The weight of each configuration depends on the set of external constraints (Table 3.2). The sum of all weights, the normalization factor, is defined as partition function, whose logarithm is the thermodynamic potential, e.g., the Helmholtz and Gibbs free energy for the canonical and the isothermal-isobaric ensembles, respectively.

Different ensembles are equivalent in the thermodynamic limit $N \to \infty$. For
instance, the isothermal-isobaric ensemble reduces to the canonical ensemble if the volume fluctuations from its most probable value are negligible. An appropriate choice of ensemble can make the solution of certain problems a lot easier to reach. When switching from one ensemble to another, the thermal quantities that fluctuate also change. Some fluctuations are obviously easier to calculate in simulation, depending on the type of phase-space sampling possible for a given system, such as fluctuations of volume versus pressure. For spin systems, two ensembles, with conserved and nonconserved magnetization, are often used. Although we use the nonconserved magnetization ensemble to study the ANNNI model, the total magnetization \( \langle M \rangle \) is still approximately zero in the modulated regime, because fluctuations away from zero are very small for the system sizes considered. For the IC model, we have to use the conserved magnetization ensemble \( (M = 0) \) to satisfy the neutralization condition of Coulomb charges. Although this choice introduces certain technical difficulty in solving the reference partition functions analytically, the problem can be numerically surmounted (Sec. 5.6.1). For particle systems, the canonical ensemble is typically used, but we use a variety of other ensembles to facilitate the access to certain quantities.

Table 3.2: Statistical ensembles of particle systems.

<table>
<thead>
<tr>
<th>Ensemble</th>
<th>Constraints</th>
<th>Fluctuations</th>
<th>r.w.</th>
<th>p.f.</th>
<th>t.p.</th>
</tr>
</thead>
<tbody>
<tr>
<td>microcanonical</td>
<td>NVE</td>
<td>( \mu pT )</td>
<td>1</td>
<td>( \Omega )</td>
<td>( -TS )</td>
</tr>
<tr>
<td>canonical</td>
<td>NVT</td>
<td>( \mu pE )</td>
<td>( e^{-\beta E} )</td>
<td>( Q )</td>
<td>( F )</td>
</tr>
<tr>
<td>isothermal-isobaric</td>
<td>( NpT )</td>
<td>( \mu VE )</td>
<td>( e^{-\beta pV} e^{-\beta E} )</td>
<td>( \Delta )</td>
<td>( G )</td>
</tr>
<tr>
<td>grand canonical</td>
<td>( \mu VT )</td>
<td>( NpE )</td>
<td>( e^{\beta \mu N} e^{-\beta E} )</td>
<td>( \Xi )</td>
<td>( -pV )</td>
</tr>
<tr>
<td>generalized</td>
<td>( \mu pT )</td>
<td>NVE</td>
<td>( e^{\beta \mu N} e^{-\beta pV} e^{-\beta E} )</td>
<td>( \Upsilon = 1 )</td>
<td>0</td>
</tr>
</tbody>
</table>

\( ^a \) relative weight of each configuration
\( ^b \) partition function
\( ^c \) thermodynamic potential
3.3 Microcanonical Ensemble

The conceptually simplest system is an isolated one, which has no particle, volume and energy exchange with its surroundings. This system is described by the microcanonical ensemble, for which all extensive quantities $N$, $V$ and $E$ are fixed. The equilibrium is characterized by the maximization of the Boltzmann entropy

$$S = k_B \ln \Omega,$$

(3.12)

where $k_B$ is the Boltzmann constant and $k_B T$ gives the order of magnitude of the thermal energy per particle at temperature $T$. The number of configurations (microstates) $\Omega(N,V,E)$ is also called density of state (DOS) at energy $E$. The fundamental assumption of statistical mechanics is the principle of equal a priori probabilities stating that an isolated system at fixed $N$, $V$, and $E$ is equally likely to be in any one of its $\Omega$ microstates [120]. It is most convenient to perform molecular dynamics (MD) simulations in the microcanonical ensemble because its evolution naturally guarantees conservation. But because keeping the energy fixed limits the extent of phase space sampling in some context, the ensemble is rarely used in Monte Carlo simulations. It is also an ensemble that is difficult to access experimentally.

3.4 Canonical Ensemble

In three dimensions (3D), the canonical partition function of the system at volume $V$ and temperature $T$ is defined as

$$Q(N,V,T) \equiv \frac{1}{N! \hbar^{3N}} \int \int d\mathbf{r}^N d\mathbf{p}^N e^{-\beta H(\mathbf{r}^N, \mathbf{p}^N)}.$$ 

(3.13)

Because classical particles are distinguishable, $N!$ arrangements of particles of the same configuration are all counted in the integral $\int \int d\mathbf{r}^N d\mathbf{p}^N e^{-\beta H(\mathbf{r}^N, \mathbf{p}^N)}$. In order to correct for this overcounting such that the formalism is consistent with the quantum
mechanics requirement of particle indistinguishability, the permutation number \( N! \) needs to be included. Otherwise, the so-called Gibbs paradox results [124]. The \( 1/h^{3N} \) factor contains Plank’s constant \( h \) and arises from the constraint that the position \( r \) and momentum \( p \) of a particle cannot simultaneously undergo arbitrarily small increments, in accordance with the uncertainty principle. In other words, as the integral is taken over the 6D phase space \((r^N, p^N)\), the resolution of the integration grid is \( h \sim \delta x \delta p \) in each dimension. To scan over all the configurations, the mathematically exact continuous integral \( \int \int \frac{dr^N dp^N}{h^{3N}} \) is physically equivalent to \( \sum_s \), where \( s \) indexes configurations in phase space, with each state occupying a small volume \( h^{3N} \). This term also makes the partition function dimensionless.

If we divide the energy space into shells with increment \( \delta E \) such that

\[
\Omega(N, V, E) = \frac{1}{N! h^{3N} \Omega(N, V, E)} \int \int \frac{dr^N dp^N}{h^{3N}} \delta(E, r^N, p^N) E < H(r^N, p^N) < E + \delta E,
\]

the canonical ensemble can be related with the microcanonical ensemble by

\[
Q = \int dE \frac{dE}{\delta E} \Omega(N, V, E) e^{-\beta E},
\]

where \( \int dE \) can be formally written as \( \sum_E \) [125].

It is often convenient to integrate out the kinetic part explicitly and write \( Q \) as

\[
Q = \frac{1}{N! \Lambda^{3N}} \int dr^N e^{-\beta U(r^N)} = \frac{Z}{N! \Lambda^{3N}},
\]

using the thermal de Broglie wavelength

\[
\Lambda = \sqrt{\frac{h^2}{2\pi mk_B T}},
\]

which is the characteristic length scale of the wavelike thermal motion of particles. When \( \Lambda \ll (V/N)^{1/3} = \rho^{-1/3} \), the average inter-particle distance, the system can
be reasonably described by classical Maxwell-Boltzmann statistics. Otherwise, the system will obey Fermi-Dirac statistics or Bose-Einstein statistics, depending on its spin quantum number. Therefore, strictly speaking, quantum statistics has to be employed at low temperatures and small length scales. But because we are concerned about colloidal particles of mesoscopic mass in soft matter systems, classical statistics is here essentially valid at all the temperatures we consider.

Because the momenta distribution of particles is decoupled from the static configuration and thus the inter-particle potential, the configuration integral

\[ Z = \int \! dr^N e^{-\beta U(r^N)} \]  

(3.18)

contains all the required information to study different phases formed. Statistically, the rates at which particles move are reflected in the quantity \( \Lambda \) (or \( T \)) but do not interfere directly with the overall frequency at which given configurations (or phases) are visited.

Because the kinetic part is trivial and the same for most systems, the partition function is therefore often decomposed as

\[ Q = \frac{V^N}{N! \Lambda^{3N}} \frac{Z}{V^N} = Q^{id} Q^{ex}, \]  

(3.19)

where the ideal gas (id) part has

\[ Q^{id} \equiv \frac{V^N}{N! \Lambda^{3N}}, \]  

(3.20)

and

\[ F^{id} \equiv -k_B T \ln Q^{id} = k_B T N \left( \ln \rho \Lambda^3 - 1 \right). \]  

(3.21)

Note that Sterling’s approximation \( \ln N! \simeq N \ln N - N \) is used to obtain this result.

At a given temperature, systems with different potentials \( U \) are therefore distinguished by the excess (ex) part \( Q^{ex} \) and \( F^{ex} = -k_B T \ln \frac{Z}{V^N} \).

29
The total internal energy is then the sum of the kinetic energy and the potential energy $\langle E \rangle = \langle K \rangle + \langle U \rangle$ with $\langle K \rangle = \frac{3}{2} N k_B T$ and

$$\langle U \rangle = \frac{1}{Z} \int d\mathbf{r}^N U e^{-\beta U}. \quad (3.22)$$

Similarly, the heat capacity can be obtained from the two independent contributions

$$C_V = \left( \frac{\partial \langle E \rangle}{\partial T} \right)_V = \frac{3}{2} N k_B + \left( \frac{\partial \langle U \rangle}{\partial T} \right)_V, \quad (3.23)$$

where the kinetic part is just a constant at fixed $T$.

From the above results, we obtain a first fluctuation relation for the canonical ensemble

$$C_V = \frac{\langle E^2 \rangle - \langle E \rangle^2}{k_B T^2}. \quad (3.24)$$

We can also study the fluctuations of the instantaneous pressure

$$\Pi = \rho k_B T + \frac{W}{3V}, \quad (3.25)$$

where the virial is defined as

$$W = - \sum_{i>j} r_{ij} \frac{du(r_{ij})}{dr_{ij}}. \quad (3.26)$$

It can then be shown that the bulk modulus (inverse compressibility) [122, 126]

$$B = \kappa^{-1} \equiv -V \left( \frac{\partial p}{\partial V} \right)_T$$

$$= \frac{2p + \rho k_B T}{3} + \langle \Theta \rangle - \frac{V}{k_B T} \langle (\delta \Pi)^2 \rangle, \quad (3.27)$$

from the pressure fluctuation

$$\langle (\delta \Pi)^2 \rangle = \langle (\Pi - \langle \Pi \rangle)^2 \rangle = \langle \Pi^2 \rangle - \langle \Pi \rangle^2, \quad (3.28)$$

and

$$\langle \Theta \rangle = \frac{1}{9V} \sum_{i>j} r_{ij}^2 \frac{d^2 u(r_{ij})}{dr_{ij}^2}. \quad (3.29)$$
3.5 Isothermal-Isobaric ensemble

The partition function of the isothermal-isobaric ensemble at temperature $T$ and pressure $p$ is

$$\Delta(N, p, T) = \frac{\beta p}{N!h^{3N}} \int_0^\infty dV e^{-\beta pV} \int \int d\mathbf{r}^N d\mathbf{p}^N e^{-\beta H(\mathbf{r}^N, \mathbf{p}^N)}$$

$$= \beta p \int_0^\infty dV e^{-\beta pV} Q(N, V, T). \quad (3.30)$$

The factor $\beta p$ makes $\Delta$ dimensionless and is added as a prefactor for similar reasons as the multiplication by $1/h^{3N}$ in $Q$. From the ideal gas law $\beta p^{id} = \rho^{id} = 1/v^{id}$, we obtain an estimate of the average volume per particle $v \sim \frac{1}{\beta p}$, which is the volume $V$ resolution in the integral. Formally, we can write $\int_0^\infty \frac{dV}{1/\beta p}$ as $\sum_V$, where the latter sum is taken over discretized $V$ with increments of $1/\beta p$.

In this ensemble, the constant pressure heat capacity can be measured from the enthalpy $(H = E + pV)$ fluctuations

$$C_p \equiv \left( \frac{\partial H}{\partial T} \right)_p = \frac{\langle H^2 \rangle - \langle H \rangle^2}{k_B T^2}. \quad (3.31)$$

Volume (instead of pressure) fluctuations provide a numerically straightforward evaluation of the compressibility [122]

$$\kappa \equiv -\frac{1}{V} \left( \frac{\partial V}{\partial p} \right)_T = \frac{\langle V^2 \rangle - \langle V \rangle^2}{k_B T \langle V \rangle}. \quad (3.32)$$

The coefficient of thermal expansion can also be calculated by the joint fluctuation of volume and enthalpy [122]

$$\alpha \equiv \frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_p = \frac{\langle VH \rangle - \langle V \rangle \langle H \rangle}{k_B T^2 \langle V \rangle}. \quad (3.33)$$
3.6 Grand Canonical Ensemble

The grand canonical partition function at temperature $T$ and chemical potential $\mu$

$$\Xi(\mu, V, T) = \sum_{N=0}^{\infty} e^{\beta \mu N} \frac{1}{N! h^3} \int d^3 r d^3 p e^{-\beta H(r, p)}$$

$$= \sum_{N=0}^{\infty} e^{\beta \mu N} Q(N, V, T) = \sum_{N=0}^{\infty} \frac{z^N}{N!} Z(N, V, T),$$

(3.34)

where we have defined the activity

$$z = e^{\beta \mu} \Lambda^3.$$

(3.35)

In this ensemble, the fluctuation of particle number provides an alternative evaluation of the compressibility

$$\kappa = \frac{V}{k_B T} \frac{\langle N^2 \rangle - \langle N \rangle^2}{\langle N \rangle^2}.$$ 

(3.36)

3.7 Generalized Ensemble

In the generalized ensemble [127, 128], only intensive parameters $\mu$, $p$, and $T$ are specified and the corresponding extensive variables $N$, $V$, and $E$ have infinite fluctuations. The partition function then trivially equal to unity

$$\Upsilon(\mu, p, T) = \sum_{N=0}^{\infty} e^{\beta \mu N} \beta p \int_0^\infty dV e^{-\beta p V} \frac{1}{N! h^3} \int d^3 r d^3 p e^{-\beta H(r, p)}$$

$$= \sum_{N=0}^{\infty} e^{\beta \mu N} \Delta(N, p, T)$$

(3.37)

$$= \beta p \int_0^\infty dV e^{-\beta p V} \Xi(\mu, V, T) = 1.$$

Although this ensemble has no experimental equivalent, it will be conceptually useful in the discussion of $[N]pT$ ensemble simulation in Sec. 5.7.
3.8 Nonequilibrium Statistical Mechanics and Shearing

All of the above discussion concerns about equilibrium thermodynamics/statistical mechanics. When a system is at equilibrium, the probability $p_{\nu}$ for it to be in a state $\nu$ and the transition probability $w_{\nu\nu'}$ to another state $\nu'$ satisfy the detailed balanced condition

$$p_{\nu}w_{\nu\nu'} = p_{\nu'}w_{\nu'\nu},$$  \hfill (3.38)

which sets the total probability flow of each state

$$\dot{p}_{\nu} = \sum_{\nu'}[-p_{\nu}w_{\nu\nu'} + p_{\nu'}w_{\nu'\nu}],$$  \hfill (3.39)

to zero.

It is quite common, however, to also observe systems that are out of equilibrium. The major consequence of having a nonequilibrium state is that the detailed balance condition is broken such that there exists no general distribution law governing the probability distribution. Despite the lack of an exact theoretical description, the possibility for a nonequilibrium system to have its state distribution disrupted can change its material structure. Shearing is often used to drive a system out of equilibrium and can cause dramatic materials changes such as viscosity thinning and thickening in colloidal dispersions [129].

It was mentioned in Sec. 1.1 that shear is often applied to order diblock copolymers. Recent simulations demonstrate that shear can induce alignment of lamellae in diblock copolymer films [130]. A Laudau-Ginzburg theory has even shown that the shear can raise the modulated-disorder transition temperature and make it less strongly first order in character [67].
One of the most astonishing phenomena in nature is the abrupt transition between different phases of the same constituent molecules. With one type of interaction and one partition function, “how do the molecule know whether they should behave as gas or liquid?” [131]. Since the partition function is analytic, where does the singular/discontinuous behavior at phase transition come from? These fundamental questions have puzzled scientists for decades.

By modifying the ideal gas law, the van der Waals equation of state takes into account the volume of molecules and their intermolecular forces. The results demonstrate that the gaseous and liquid states are in fact of the same translational symmetry and merge into each other continuously at temperatures above a special point, the critical point (Fig. 4.1) [132]. The van der Waals theory is mean-field like [124, 133], treating all the particles equally and neglecting spatial fluctuations. Many other mean-field formulations, such as the Bragg-Williams theory of the Ising ferromagnet[134] and the Landau phenomenological theory [135], share the same phenomenology.

The Mayer cluster expansion method was the first discussion of phase transitions
Figure 4.1: Isotherms of the van der Waals equation \( \left( \frac{p}{p_c} + \frac{3}{(v/v_c)^2} \right) (3v/v_c - 1) = 8T/T_c \) rescaled by the critical quantities \( p_c, v_c \) and \( T_c \). Unphysical van der Waals loops exist for \( T < T_c \). The real coexisting densities (black dots) are determined by the Maxwell construction, which equates the areas \( A \) and \( B \) enclosed by the loop with the horizontal dashed line, as for \( T = 0.9T_c \) and \( p_{coex} = 0.647p_c \), corresponding to equating the chemical potential of both phases in equilibrium.

Beyond mean-field theory. It predicted the condensation of a gas into a liquid and provided the microscopic explanation for the Maxwell construction of the van der Waals loop [136, 137] (Fig. 4.1). This perturbation idea was also used in various versions of series expansions [138] and virial expansions [120]. Using infinite series, Yang and Lee later on proved rigorously the existence of singularity at phase transitions in the thermodynamic limit [139].

Another celebrated triumph of the theoretical solution of phase transitions is the renormalization group (RG) theory that explains the singular critical regime [140, 141]. Different systems have the same scaling behavior, or universality, at the critical point and RG explains why the microscopic details are of secondary importance. The correlation length diverges, and therefore the RG flow in the coupling constant space determines the universality of the transition.
With experimental advances, a growing number of exotic phases have emerged and theoretical developments have followed in step. To study phases with an inhomogeneous spatial distribution of matter, density functional theory (DFT) was developed [142]. It treats the nonuniform phase with a spatially varying density profile and minimizes a Landau-type free energy to obtain the system’s equilibrium properties. With the aid of self-consistent numerical computations, this method has been used extensively, notably in the study of block copolymers [113], which is a canonical problem in soft matter.

Based on our knowledge of equilibrium thermodynamics and statistical mechanics, the rest of this chapter will discuss the stability and transitions of different phases that occur in our systems of interest. Structure factors and order parameters that quantitatively capture the emergence of phases will first be introduced, followed by a general discussion of the two types of phase transitions. We will then use theoretical methods, such as mean-field theory, high temperature series expansion, and cell model, to begin the analysis of the phase transitions in various systems.

4.1 Structure Factor and Order Parameters

4.1.1 Liquid Structure Factor and Radial Distribution Function

Before embarking on a discussion of phase transitions, we first introduce quantities that characterize the emergence of phases, also known as order parameters. In liquid theory, the Fourier transform

$$\hat{\rho}_k = \int \rho(r) e^{-ik \cdot r} dr = \sum_{i=1}^{N} e^{-ik \cdot r_i}$$

(4.1)

of the microscopic density

$$\rho(r) = \sum_{i=1}^{N} \delta(r - r_i)$$

(4.2)

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extracts periodic structure of the density profile at wave vector \( k \). The \textit{structure factor} of a \( N \)-particle system is then defined as \([143]\)

\[
S(k) \equiv \left\langle \frac{1}{N} \hat{\rho}_k \hat{\rho}_{-k} \right\rangle = \frac{1}{N} \sum_{i=1}^{N} \sum_{j=1}^{N} e^{-ik \cdot r_i} e^{ik \cdot r_j} \] \tag{4.3}

\[
= \frac{1}{N} \left\langle \left| \sum_{i=1}^{N} \cos(k \cdot r_i) \right|^2 + \left| \sum_{i=1}^{N} \sin(k \cdot r_i) \right|^2 \right\rangle.
\]

Under this definition, \( \sqrt{S(k)/N} \) is normalized for the modulated phases.

The structure factor is directly measurable by experimental techniques such as X-ray, neutron or visible light diffraction, depending on the length scale of the particles. If the structure factor \( S(k) \) is drawn as a function of \( k = |k| \), its main peak reflects the short-range order in the system. For instance, \( S(k) \) mainly peaks at \( k \sim 2\pi/\sigma \) for a dense fluid, where \( \sigma \) is the molecular diameter. For an ideal gas, the peak only occurs at \( k = 0 \) indicating that the particle length scale has disappeared in such a system. For microphases, we expect \( S(k) \) to have its dominant peak at the wave vector corresponding to the pattern length on a mesoscopic length scale.

Another useful quantity characterizing the local order is the \textit{radial distribution function}

\[
g(r) = \frac{1}{\rho} \left\langle \sum_{j \neq i}^{N} \delta(r - r_{ij}) \right\rangle, \tag{4.4}
\]

which is related to the structure factor by

\[
S(k) = 1 + \rho \int g(r) e^{-ik \cdot r} dr. \tag{4.5}
\]

The particle indices \( i \) can be for any one of the \( N \) particles if the system is strictly homogenous. When the system is isotropic, \( g(r) = g(r) \) and

\[
g(r) = \frac{1}{\rho} \frac{n(r)}{4\pi r^2} dr, \tag{4.6}
\]

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where $n(r)$ is the number of particles at a distance between $r$ and $r + dr$ from a given particle.

The radial distribution function $g(r)$ modulates the overall global density $\rho$ in space. For an ideal gas or for a liquid at $r \to \infty$, $g(r) = 1$, which indicates the absence of long-range order. For solids, $g(r)$ peaks at certain specific positions corresponding to different lattice spacings. For hardcore particles of diameter $\sigma$, $g(r) = 0$ for $r < \sigma$. For softcore particles, such as GEM-$n$ and PSM, $g(r) \neq 0$ at $r = 0$ which is the particle overlap signature of clustering.

If the system is homogeneous, $g(r)$ can be used to evaluate thermal quantities via integrals, which is quite useful in simulations conducted at fixed $V$. For instance, the pressure

$$p = \rho k_B T - \frac{\rho^2}{6} \int \mathbf{r} \cdot \nabla u(\mathbf{r}) g(\mathbf{r}) d\mathbf{r}$$

$$= \rho k_B T - \frac{\rho^2}{6} \int_0^\infty r \frac{du(r)}{dr} g(r) 4\pi r^2 dr$$

$$= \rho k_B T - \frac{2\pi \rho^2}{3} \int \frac{du(r)}{dr} g(r) r^3 dr,$$

and the potential energy

$$\frac{U}{N} = \frac{1}{2} \int_0^\infty u(r)\rho g(r) 4\pi r^2 dr.$$ (4.8)

Special care needs to be taken if the inter-particle potential $u(r)$ is singular or discontinuous at certain distance (Appendix A). For the HS of diameter $\sigma$, for instance,

$$p_{HS} = \rho k_B T + \frac{2\pi \rho^2 k_B T}{3} \sigma^3 g_+(\sigma),$$ (4.9)

while for the PSM of diameter $\sigma$,

$$p_{PSM} = \rho k_B T + \frac{2\pi \rho^2 k_B T}{3} \sigma^3 [g_+(\sigma) - g_-(\sigma)]$$ (4.10)
and for the SW of hardcore diameter $\sigma$ and attraction range $\lambda\sigma$,

$$p_{SW} = \rho k_B T + \frac{2\pi\rho^2 k_B T}{3} \left[ \sigma^3 g_+(\sigma) - \lambda^3 \sigma^3 g_-(\lambda\sigma) + \lambda^3 \sigma^3 g_+(\lambda\sigma) \right]. \quad (4.11)$$

The upper/lower limit $g_+(x)/g_-(x)$ must be separately computed when $g(r)$ is discontinuous at $r = x$.

4.1.2 Spin Magnetization as Order Parameter

For the homogeneous Ising model, the average magnetization $\langle m \rangle = \langle \sum_i s_i \rangle / N$ is used as the order parameter, characterizing the transition from a ferromagnetic phase to a paramagnetic phase, as $T$ goes above the critical temperature. To describe spatially modulated phases of spin models, functions of the Fourier spin density,

$$\tilde{s}_q \equiv \sum_{i=1}^{N} s_i e^{i2\pi q z_i}, \quad (4.12)$$

similar to $\hat{\rho}(k)$ used in particle systems, are natural choices for characterizing modulations in layered systems$^1$. The simplest of them, the generalized magnetization per spin, is defined analogously to the absolute magnetization in the Ising model [6]

$$\langle m(q) \rangle = \frac{1}{N} \sqrt{\langle \tilde{s}_q \rangle \langle \tilde{s}_{-q} \rangle}$$

$$= \frac{1}{N} \sqrt{\left\langle \sum_i s_i \cos(q z_i) \right\rangle^2 + \left\langle \sum_i s_i \sin(q z_i) \right\rangle^2}. \quad (4.13)$$

A direct use of $\langle m(q) \rangle$, however, causes problems in long simulations, because in principle it averages to zero as the lattice drifts along the $z$ direction, eventually recovering translational symmetry (Fig. 4.2). Maximizing the real component of $\tilde{s}_q$ with respect to a phase shift in the $z$ direction for each configuration before taking

$^1$ Note that here we use the wave number $q = k/2\pi$ to be consistent with the custom of the lattice model community.
the thermal average resolves this issue. In practice, a straightforward parabolic interpolation scheme is sufficient [144]. Using the optimized version of $\langle m(q) \rangle$, even in simulations that are too short for the system’s periodicity to completely diffuse, significantly improves the data quality (Fig. 4.2). Only quantities based on optimized $\tilde{s}_q$ are therefore used in the rest of this work.

The next higher magnetization moment, the $z$-axial static structure factor, is similar to the equivalent liquid-state quantity $S(k)$

$$NS(q) \equiv \langle \tilde{s}_q \tilde{s}_{-q} \rangle = N^2 \langle m^2(q) \rangle$$

$$= \left\langle \left( \sum_i s_i \cos(qz_i) \right)^2 + \left( \sum_i s_i \sin(qz_i) \right)^2 \right\rangle,$$

(4.14)

where $\langle m^2(q) \rangle$ is the second moment of the magnetization [5, 10]. Both $S(q)$ and its normalized version $\sqrt{S(q)/N} = \sqrt{\langle m^2(q) \rangle}$ [6] grow upon cooling and are maximal at the wave number $q_c$ of the first modulated phase below $T_c$. 

Figure 4.2: Optimized and un-optimized $\langle m(q) \rangle$ and $\sqrt{S(q)/N}$ for the ANNNI model at $\kappa = 0.7$ and $q_c = 0.1917$. The difference between $S(q)/N$ and $\langle m(q) \rangle^2$ gives $\chi(q)$ (Eq. 5.87).
4.2 Second-Order Phase Transition and Critical Exponents

During a second-order phase transition, one phase changes to another continuously without releasing latent heat [133, 145]. The specific phase point/line on a $p$-$T$ phase diagram where second-order phase transitions occur is the critical point (CP)/$\lambda$-line. At the CP, the correlation length $\xi$ diverges, fluctuations become infinite and the two phases about to separate are indistinguishable. Different transitions can be categorized in universality classes that share similar critical properties. Each universality class is characterized by a set of critical exponents, describing the asymptotical/divergent behaviors of thermal quantities as functions of the reduced temperature $t = \frac{T - T_c}{T_c}$ (Table 4.1). For instance, the correlation length $\xi$ diverges as

$$\xi \sim |t|^{-\nu}, \quad \nu > 0; \quad (4.15)$$

the order parameter approaches zero asymptotically as, e.g. magnetization for spin systems,

$$m \sim |t|^{\beta}, \quad \beta > 0, \quad (4.16)$$

or coexistence densities for liquid-gas (l-g) transition,

$$\rho_l - \rho_g \sim |t|^{\beta}, \quad \beta > 0; \quad (4.17)$$

the response function of the order parameter, susceptibility $\chi$ for spin systems and compressibility $\kappa$ for fluid systems, diverges as

$$\chi \sim |t|^{-\gamma}, \quad \gamma > 0; \quad (4.18)$$

and the heat capacity changes as

$$C_V \sim |t|^{-\alpha}. \quad (4.19)$$

A special type of critical points is found at a Lifshitz point (LP) where three phase boundaries meet [47, 65]. The LP is a multicritical point in a sense that more
Table 4.1: Critical exponents values of various universality class.

<table>
<thead>
<tr>
<th>Exponent</th>
<th>Ising (mean field)</th>
<th>3D Ising</th>
<th>3D XY</th>
<th>3D Lifshitz</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\alpha$</td>
<td>0$^c$</td>
<td>0.11</td>
<td>-0.01$^d$</td>
<td>0.18(2)</td>
</tr>
<tr>
<td>$\beta$</td>
<td>1/2</td>
<td>0.34</td>
<td>0.35</td>
<td>0.238(5)</td>
</tr>
<tr>
<td>$\gamma$</td>
<td>1</td>
<td>1.24</td>
<td>1.32</td>
<td>1.36(3)</td>
</tr>
<tr>
<td>$\nu$</td>
<td>1/2</td>
<td>0.63</td>
<td>0.67</td>
<td>0.33(3)$^e$</td>
</tr>
</tbody>
</table>

$^a$ Ref. [146].
$^b$ Ref. [2].
$^c$ $C_V$ is discontinuous
$^d$ $C_V$ has a finite cusp
$^e$ Ref. [1].

than two of the phase boundaries are of second order. If the anisotropy of the phase, say along two directions $\parallel$ and $\perp$, are encountered at the LP, the correlation length may then diverge with different critical exponents

$$\xi_{\parallel} \sim |t|^{-\nu_{\parallel}}, \quad \xi_{\perp} \sim |t|^{-\nu_{\perp}}.$$  \hspace{1cm} (4.20)

Note that the critical exponents are not all independent, as all the singular behaviors are essentially a result of the divergence of $\xi$ as $T \to T_c$. Different scaling laws thus relate critical exponents. The Rushbrooke scaling law [147, 148]

$$\alpha + 2\beta + \gamma = 2, \quad (4.21)$$

and the Josephson scaling relation, or the hyperscaling relation, which involves the dimension of space $d$,

$$2 - \alpha = d\nu, \quad (4.22)$$

are examples of such laws.

---

$^2$ However, $\xi$ is not the only length scale that enters the dimensional analysis of critical thermal variables. Another microscopic length scale leading to the anomalous dimension $\theta$ may also play a role, which make it possible for the critical exponents to differ from their mean-field values [141].
4.3 First-Order Phase Coexistence and Isostructural Transition

When a first-order phase transition occurs, the two coexisting phases 1 and 2 may be thought of as two equilibrium systems in contact, and therefore satisfy the necessary conditions

\[ T_1 = T_2, \quad p_1 = p_2, \quad \mu_1 = \mu_2. \quad (4.23) \]

Because \( \mu = \mu(p, T) \), only two of the above three conditions are independent, i.e. any two conditions at coexistence will automatically imply the third one, in agreement with the Gibbs’ phase rule discussed in Chapter 3.

As \( p \) or \( T \) changes, the free energy curve develops a cusp at the first-order transition, corresponding to a jump in \( V \) or \( S \). On the \( F-V \) (\( F-\rho \)) plane, the Helmholtz free energy curve has a double-well shape if the metastable regime is included. The real equilibrium \( F \) curve in the coexistence region is a line that is tangent to both wells at corresponding coexisting volumes (Fig. 4.3).

Because the curvature of the original Helmholtz free energy at coexistence is often too small to be visualized, a transformed free energy \( \tilde{f} = f \rho - K \rho \) is used instead.
By an appropriate choice of constant $K$, the curvature can be enhanced [15]. The phase coexistence at a specified $T$ is then obtained by common tangent construction of $\tilde{f}(\rho)$ because

$$\left( \frac{\partial \tilde{f}}{\partial \rho} \right)_T = \left( \frac{\partial f}{\partial \rho} \right)_T \rho + f - K = p/\rho + f - K = \mu - K,$$

and so a common tangent construction means equating the chemical potential.

In order to better trace the coexistence line on the phase diagrams, its slope can be calculated at a few points. For the $p$-$T$ projection, the standard Clausius-Clapeyron relation can be used

$$\left( \frac{\partial p}{\partial T} \right)_{\text{coex}} = \frac{\Delta s}{\Delta v},$$

where $\Delta v$ and $\Delta s$ are, respectively, the per particle volume and entropy difference between the two phases across the transition. For the $T$-$\rho$ projection, each phase has a separate relation for its slope, namely

$$\left( \frac{\partial \rho}{\partial T} \right)_{\text{coex}} = -\rho \alpha + \rho \kappa \left( \frac{\partial p}{\partial T} \right)_{\text{coex}}.$$

### 4.3.1 Isostructural Transition

On the $T$-$\rho$ phase diagram of simple liquids interacting with relatively long-range attractions, the first-order coexistence between the gas and the liquid terminates at a critical point. Analogous transitions have been observed between two solid phases of the same crystal structure. Because the two phases share the same breaking of translational symmetry, this transition is referred to as an **isostructural transition**.

Isostructural transitions were first observed in the cerium (Ce) phase diagram, which presents a loosely packed FCC solid coexisting with a densely packed FCC solid [149, 150]. Schematically, the quantum mechanical core collapse of Ce was
modeled by a core-softened hard sphere potential (or hard sphere soft core potential),
which has two length scales leading to the two types of lattice spacing [149, 150].

Similarly, in model short-range attractive systems, isostructural transitions have
also been observed [151]. As the attraction range decreases, the phase diagram
develops a solid-solid isostructural transition at high density from the liquid-gas
transition [152–154].

4.4 Mean-Field Theory

Other than for a small number of exactly solvable models, such as the 2D Ising
model, mean-field theory is often the only analytically possible way to estimate a
system’s phase behavior. Because it ignores fluctuations and thus underestimates
the entropic contribution, mean-field theory tends to overestimate transition tem-
peratures. Despite this drawback, mean-field theory provides qualitative correct
predictions to most models, and in certain cases, such as transitions dominated by
energy, mean-field description are nearly exact. In this section, we briefly review the
mean-field behavior of the order-disorder transition of the ANNNI [13, 155] and the
IC model [7].

4.4.1 Mean-Field Theory of the ANNNI Model

The energy of the spin 0 is

\[ E_0 = -J \left[ \sum_{i=1}^{4} s_0 s_i + \sum_{i=5}^{6} s_0 s_i \right] + \kappa J \sum_{i=7}^{8} s_0 s_i, \]  

(4.26)

where the three summations are taken over the four nearest neighbors in the \( xy \) plane,
the two nearest neighbors in the \( z \) direction and the two next-nearest neighbors in
the \( z \) direction, respectively. If the average magnetization at site 0 is denoted as
\( \langle s_0 \rangle \), then, in the mean-field approximation, the average magnetization at any other
site $i$ can be written as

$$\langle s_i \rangle = \langle s_0 \rangle \cos(kz), \quad (4.27)$$

which is modulated by the sinusoidal function of periodicity $k$ along the $z$ direction. Substituting Eq. 4.27 into Eq. 4.26, we obtain the mean-field energy

$$E_0^{MF} = -\Delta H(k) \langle s_0 \rangle, \quad (4.28)$$

where

$$\Delta H(k) = [4J + 2J \cos k - 2\kappa J \cos 2k] \langle s_0 \rangle \quad (4.29)$$

is the effective field applying on spin 0.

The equilibrium periodicity $k_c$ at the order-disorder transition occurs when $E_0^{MF}$ is minimized. By setting $\partial E_0^{MF}/\partial k = 0$, we get

$$\sin k(1 - 4\kappa \cos k) = 0, \quad (4.30)$$

which gives three minima

$$k_c = 0 \quad , \quad E_0^1 / J \langle s_0 \rangle^2 = 2\kappa - 6,$$
$$k_c = \pi \quad , \quad E_0^2 / J \langle s_0 \rangle^2 = 2\kappa - 2,$$
$$k_c = \cos^{-1} \left( \frac{1}{4\kappa} \right) \quad , \quad E_0^3 / J \langle s_0 \rangle^2 = -4 - \frac{1}{4\kappa} - 2\kappa, \quad \kappa \geq 0.25. \quad (4.31)$$

After comparing the three energy minima, we can extract the equilibrium periodicity

$$k_c^{MF}(\kappa) = \begin{cases} 0 & , \quad 0 \leq \kappa \leq 0.25 \\ \cos^{-1} \left( \frac{1}{4\kappa} \right) & , \quad \kappa \geq 0.25 \end{cases} \quad (4.32)$$

and recognize the Lifshitz point at $\kappa_L^{MF} = 0.25$, beyond which the modulation emerges.

For mean-field spins, the average magnetization per spin is expressed as [156]

$$\langle s_0 \rangle = \tanh (\beta \Delta H), \quad (4.33)$$
and the order-disorder transition is determined by

$$\beta_c^{\text{MF}} \frac{\Delta H(q_c^{\text{MF}})}{\langle s_0 \rangle} = 1. \quad (4.34)$$

From Eq. 4.29, Eq. 4.32 and Eq. 4.34, we therefore obtain the transition temperature

$$k_B T_c^{\text{MF}}(\kappa)/J = \begin{cases} 
6 - 2\kappa & , \ 0 \leq \kappa \leq 0.25 \\
4 + 2\kappa + \frac{1}{4\kappa} & , \ \kappa \geq 0.25
\end{cases} \quad (4.35)$$

### 4.4.2 Mean-Field Theory of the IC Model

The details of this derivation are given in Appendix B, but we here present the highlights of the work. We first rewrite the Hamiltonian of the 3D IC model as

$$H_{1C} = \frac{J}{2} \sum_{i=1}^{N} s_i \sum_{\Delta_i \in \text{NN}} (-s_{\Delta_i}) + \frac{Q}{2} \sum_{i \neq j} s_i s_j \frac{1}{r_{ij}} = \frac{J}{2} \sum_{i=1}^{N} \sum_{j=1}^{N} V_{ij} s_i s_j. \quad (4.36)$$

where $\Delta_i \in \text{NN}$ indexes spins that are nearest-neighbor (NN) to spin $i$ and interactions are grouped into one pair potential

$$V_{ij} = \begin{cases} 
0 & , \ i = j \\
-1 + \frac{Q}{J} \frac{1}{r_{ij}} & , \ \langle i, j \rangle \\
\frac{Q}{J} \frac{1}{r_{ij}} & , \ \text{others}
\end{cases} \quad (4.37)$$

After introducing the lattice Fourier transform pair [65]

$$\hat{S}(\mathbf{k}) = \frac{1}{\sqrt{N}} \sum_{i=1}^{N} s_i e^{i\mathbf{k} \cdot \mathbf{r}_i}, \quad \hat{V}(\mathbf{k}) = \frac{1}{N} \sum_{i=1}^{N} \sum_{j=1}^{N} V_{ij} e^{i\mathbf{k} \cdot (\mathbf{r}_i - \mathbf{r}_j)}, \quad (4.38)$$

$$s_i = \frac{1}{\sqrt{N}} \sum_{\mathbf{k} \in \text{BZ}} \hat{S}(\mathbf{k}) e^{-i\mathbf{k} \cdot \mathbf{r}_i}, \quad V_{ij} = \frac{1}{N} \sum_{\mathbf{k} \in \text{BZ}} \hat{V}(\mathbf{k}) e^{-i\mathbf{k} \cdot (\mathbf{r}_i - \mathbf{r}_j)}, \quad (4.39)$$

where the sum of wave vectors is taken over the first Brillouin zone (BZ), we can express the Hamiltonian in Fourier space

$$H_{1C} = \frac{J}{2} \sum_{\mathbf{k}} \hat{V}(\mathbf{k}) \left| \hat{S}(\mathbf{k}) \right|^2. \quad (4.40)$$
It can be shown that if the Fourier transform is done on the Ising and Coulomb parts respectively, then

\[ H_I = -J \sum_k \sum_{\alpha=x,y,z} \cos k_{\alpha} |\hat{S}(k)|^2, \quad (4.41) \]

and

\[ H_C = \frac{Q}{2} \left[ 4\pi \sum_k \frac{|\hat{S}(k)|^2}{2 \sum_{\alpha}(1 - \cos k_{\alpha})} - v(0) \sum_k |\hat{S}(k)|^2 \right], \quad (4.42) \]

where

\[ v(r) = \frac{1}{|r|} = \frac{4\pi}{N} \sum_k \frac{e^{-ik \cdot r}}{2 \sum_{\alpha}(1 - \cos k_{\alpha})}, \quad (4.43) \]

is expressed using lattice Green’s functions [157], and in particular \( v(0) = 0.25273100986 \).

By equating \( H_{IC} = H_I + H_C \) and comparing with Eq. 4.40, we recognize that

\[ \hat{V}(k) = -2 \sum_{\alpha=x,y,z} \cos k_{\alpha} + \frac{4\pi Q}{J} \left( \frac{1}{2 \sum_{\alpha}(1 - \cos k_{\alpha})} - v(0) \right) \]

\[ = h(k) + \frac{4\pi Q}{J} \left( \frac{1}{h(k)} - v(0) \right) - 6, \quad (4.44) \]

where \( h(k) = 2 \sum_{\alpha}(1 - \cos k_{\alpha}) = 6 - \cos k_x - \cos k_y - \cos k_z \geq 0 \).

Minimizing the energy with respect to the periodicity, \( \frac{\partial \hat{V}(k)}{\partial h(k)} = 1 - \frac{4\pi Q}{J} \frac{1}{h(k)^2} = 0 \),

leads to \( h(k_c) = 2\sqrt{\frac{\pi Q}{J}} \), which provides the equilibrium modulation at the order-disorder transition

\[ k_c = (\pm \arccos \left( 1 - \sqrt{\frac{\pi Q}{J}} \right), \ 0, \ 0), \ 0 \leq Q \leq 1. \quad (4.45) \]

The mean-field Hamiltonian is

\[ H_{IC}^{MF} = \frac{J}{2} \sum_i \sum_j V_{ij} \langle s_i \rangle \langle s_j \rangle = -\frac{1}{2} \sum_i \langle s_i \rangle \left[ -J \sum_j V_{ij} \langle s_j \rangle \right] = -\frac{1}{2} \sum_i \langle s_i \rangle \Delta H_i, \quad (4.46) \]
where the effective field
\[ \Delta H_i = -J \sum_j V_{ij} \langle s_j \rangle \] (4.47)
becomes in Fourier space
\[ \Delta \hat{H}(k) = -J \hat{V}(k) \hat{m}(k), \] (4.48)
with \( \hat{m}(k) = \frac{1}{\sqrt{N}} \sum_j \langle s_j \rangle e^{i k \cdot r_j} \). Similarly, the mean-field phase transition condition \( k_B T_c \langle s_i \rangle = \Delta H_i \) is Fourier-transformed into
\[ k_B T_c \hat{m}(k_c) = -J \hat{V}(k_c) \hat{m}(k_c), \] (4.49)
where the equilibrium \( k_c \) was obtained in Eq. 4.45. Substituting \( \hat{V}(k_c) \) with \( h(k_c) = 2 \sqrt{\frac{\pi Q}{J}} \) into Eq. 4.49, the mean-field order-disorder transition temperature is obtained
\[ k_B T_c(Q) = 6J - 4\sqrt{\pi QJ} + 4\pi Q v(0). \] (4.50)

4.5 High Temperature Series Expansion (HTSE)

Because mean-field theory neglects fluctuations, which are actually infinite at a critical point, its estimation of critical quantities often deviate quite a bit from the exact values. During the 1950s, an alternative approach, the series expansion (SE) method, was developed to accurately measure critical properties [138]. The method expands the partition function in power series around \( T = \infty \) (HTSE) or \( T = 0 \) (LTSE), and extrapolates to locate the singularity of the series, which corresponds to the phase transition point. The reason for the success of the method, which uses only the first few terms of a continuous power series seemingly hopeless for predicting a singularity, lies in the rapid convergence of the expansion toward a regular sequence [158].

In this section, we aim to review the high temperature series expansion (HTSE) of the ANNNI model, which provides fantastically accurate results of the transition temperature \( T_c \) and qualitatively reasonable prediction for the critical exponent \( \gamma \) [3, 10, 159].
4.5.1 HTSE of the Ising Model

Let’s first familiarize ourselves with the notation used in the HTSE of the Ising model with the Hamiltonian \[ \mathcal{H} = -J \sum_{\langle i,j \rangle} s_i s_j - H \sum_i s_i. \] (4.51)

We first define
\[
K = \frac{J}{k_B T} \\
w = \tanh K \\
N = zN/2 \\
M = \sum_i s_i.
\]

Here, \( z = 6 \) is the coordination number on the simple cubic (SC) lattice and \( N \) is the total number of interacting pairs \( \langle i, j \rangle \). The partition function is thus expanded as
\[
Q = \sum_{\{s_i\} = \pm 1} e^{K \sum_{\langle i,j \rangle} s_i s_j} e^{-H \sum_i s_i} = \sum_{\{s_i\} = \pm 1} \prod_{\langle i,j \rangle} e^{Ks_i s_j} \prod_i e^{L s_i}
\]
\[
= \sum_{\{s_i\} = \pm 1} \prod_{\langle i,j \rangle} \cosh K(1 + s_i s_j w) \prod_i \cosh L(1 + s_i t) \tag{4.52}
\]
\[
= (\cosh K)^N (\cosh L)^N \sum_{\{s_i\} = \pm 1} \prod_{\langle i,j \rangle} (1 + s_i s_j w) \prod_i (1 + s_i t),
\]
where we have used the relation
\[
e^{\mu K} = \cosh K + \mu \sinh K = \cosh K(1 + \mu \tanh K) = \begin{cases} e^K & , \mu = 1 \\ e^{-K} & , \mu = -1 \end{cases}. \tag{4.53}
\]

The term \( \prod_{\langle i,j \rangle} (1 + s_i s_j w) \) is the product of \( N \) terms of the form \( 1 + s_i s_j w \), each contributing either 1 or \( s_i s_j w \). We thus have
\[
\prod_{\langle i,j \rangle} (1 + s_i s_j w) = 1 + \underbrace{s_i s_j w + s_m s_n w + \cdots + (s_i s_j)(s_m s_n)w^2 + \cdots + \cdots}_{N \text{ terms}} + \underbrace{s_i s_j w + s_i s_j w + \cdots + s_i s_j w}_{N(N-1)/2 \text{ terms}} \tag{4.54}
\]
\[
= 1 + (s_i s_j)_1 w + (s_i s_j)_2 w^2 + \cdots + \sum_{r=0}^N (s_i s_j)_r w^r,
\]
where \((s_is_j)_r = \sum_{(i,j)} \sum_{(m,n)} \cdots \sum_{(p,q)} (s_is_j)(s_ms_n) \cdots (s_ps_q)\). Similarly,

\[
\prod_i (1 + s_it) = \sum_{l=0}^{N} (s_it)^l,
\]

where \((s_i)_l = \sum_i \cdots \sum_{j} s_is_j \cdots s_k\), and therefore,

\[
\prod_{(i,j)} (1 + s_is_jw) \prod_i (1 + s_it) = \sum_{l=0}^{N} \left[ \sum_{r=0} (s_is_j)_r w^r \right] (s_it)^l
\]

\[
= 1 + \left( \sum_{r=0} w^r (s_is_j)_r \right) \sum_p s_pt + \left( \sum_{r=0} w^r (s_is_j)_r \right) \sum_{p,q} s_ps_q t^2 + \cdots
\]

Considering the sum \(\sum_{(s_i) = \pm 1}\) at the front and the following relation

\[
\sum_{s_i = \pm 1} s_i^n = \begin{cases} 
2 & , \ n \text{ even} \\
0 & , \ n \text{ odd}
\end{cases}
\]

all the terms in I vanish in the calculation of \(Q\). Each term in the expansion of II can be represented by a graph that has \(r\) edges connecting certain nearest-neighbor vertices (we denote their set by \(\mathbb{V}\)) and two other arbitrary vertices \(p\) and \(q\). The number of edges that connect to a vertex gives its degree. If the \(r\) edges in a configuration are placed such that only two vertices in \(\mathbb{V}\) are of odd degree, then \(p\) and \(q\) can be chosen to be the two odd-degree vertices such that in the end all vertices appear an even number of times. Such a configuration is called a magnetic configuration (Fig. 4.4), and contributes to \(Q\). If \(d_r\) is the number of magnetic configurations with
Figure 4.4: Examples of magnetic configurations with different edge number $r$. It can be shown that $d_1 = 3N$, $d_2 = 15N$, $d_3 = 75N$, $d_4 = 363N$, $d_5 = 1755N + 9N^2$.

$r$ nearest-neighbor connecting edges, then

$$Q = 2^N (\cosh K)^{\mathcal{A}} (\cosh L)^{\mathcal{N}} \left[ 1 + \left( \sum_{r=1}^{N} d_r w^r \right) t^2 + \cdots \right]$$

$$= 2^N (\cosh K)^{\mathcal{A}} (\cosh L)^{\mathcal{N}} \Lambda_N(w,t)$$

$$= 2^N (\cosh K)^{\mathcal{A}} (\cosh L)^{\mathcal{N}} \Lambda(w,t)^N.$$  

(4.58)

The implicitly defined function $\Lambda_N(w,t)$ depends on $N$ in the form of the exponential of an intensive function $\Lambda(w,t)$, because $\ln Q$ is extensive. We first expand $\Lambda_N(w,t)$ in series of $t$

$$\Lambda_N(w,t) = 1 + a_1(N,w)t + a_2(N,w)t^2 + \cdots + a_l(N,w)t^l, \quad (4.59)$$

whose coefficients are expanded in a series of $N$

$$a_l(N,w) = b_{l,1}(w)N + b_{l,2}(w)N^2 + \cdots + b_{l,l}(w)N^l. \quad (4.60)$$

Doing a Taylor expansion, we obtain

$$\Lambda_N(w,t) = \Lambda(w,t)^N = e^{N\ln \Lambda} = 1 + N \ln \Lambda + \frac{1}{2!}(N \ln \Lambda)^2 + \cdots, \quad (4.61)$$

where

$$\ln \Lambda(w,t) = c_1(w)t + c_2(w)t^2 + \cdots + c_l(w)t^l, \quad (4.62)$$
and comparing the two expansions, we recognize
\[ c_1(w) = b_{l,1}(w). \]  
(4.63)

Differentiating
\[ \ln Q = N \ln 2 + N \ln \cosh K + N \ln \cosh L + N \ln \Lambda(w, t) \]  
(4.64)
then gives the susceptibility
\[ \chi = \frac{k_B T}{N} \frac{\partial^2 \ln Q}{\partial H^2} \bigg|_{H=0} \]  
\[ = \frac{1}{k_B T}(1 + 2c_2(w)) = \frac{1}{k_B T}(1 + 2b_{2,1}(w)) = \frac{1}{k_B T}\chi_{\text{series}}(w). \]  
(4.65)

In general \( d_r \) is a function of \( N \) and \( N^2 \), because
\[ a_2(N, w) = b_{2,1}(w)N + b_{2,2}(w)N^2 = \sum_{r=1}^{\infty} d_r w^r. \]  
(4.66)
We can identify \( b_{2,1}(w) \) from the terms of \( d_r \) that are linear in \( N \), and in the end, for the 3D Ising model (Fig. 4.4), we get
\[ \chi_{\text{series}}(w) = 1 + 6w + 30w^2 + 150w^3 + 726w^4 + 3510w^5 + \cdots \]  
(4.67)

4.5.2 HTSE of the ANNNI Model

For the ANNNI model with the Hamiltonian [10, 159]
\[ \mathcal{H} = -J_{xy} \sum_{\langle i,j \rangle} s_i s_j - J_z \sum_{\langle i,j \rangle} s_i s_j - J'_z \sum_{[i,j]} s_i s_j, \]  
(4.68)
we use the following notation
\[ K_0 = \frac{J_{xy}}{k_B T}, \quad K_1 = \frac{J_z}{k_B T}, \quad K_2 = \frac{J'_z}{k_B T}, \quad w_0 = \tanh K_0, \quad w_1 = \tanh K_1, \quad w_2 = \tanh K_2, \quad N_{xy} = 2N, \quad N_z = N, \quad N'_z = N. \]  
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In the series expansion, the indices \( l, j, k \) have the following meaning:

- \( l - j - k \) : number of NN bonds in the \( xy \) direction
- \( j \) : number of NN bonds in the \( z \) direction
- \( k \) : number of NNN bonds in the \( z \) direction,

where a bond is an edge connecting two vertices in the graph corresponding to a magnetic configuration.

For \( T > T_c \), \( \langle M \rangle = 0 \) and \( \chi = \frac{\beta}{N} \langle M^2 \rangle = \frac{\beta}{N} \sum_i \sum_j s_i s_j \), so

\[
k_B T \chi = 1 + \frac{1}{N} \sum_{\nu} \left( \sum_{i \neq j} s_i s_j \right) e^{-\beta \mathcal{H}_\nu} \frac{1}{Q}, \tag{4.69}
\]

where

\[
\sum_{\nu} \left( \sum_{i \neq j} s_i s_j \right) e^{-\beta \mathcal{H}_\nu} = \sum_{\{s_i\}} \left( \sum_{i \neq j} s_i s_j \right) e^{K_0 \sum_{(i,j)} s_i s_j} e^{K_1 \sum_{(i,j)} s_i s_j} e^{K_2 \sum_{[i,j]} s_i s_j}
\]

\[
= \sum_{\{s_i\}} \left( \sum_{i \neq j} s_i s_j \right) \prod_{\langle i,j \rangle} e^{K_0 (1 + s_i s_j w_0)} \prod_{\langle i,j \rangle} e^{K_1 (1 + s_i s_j w_1)} \prod_{[i,j]} e^{K_2 (1 + s_i s_j w_2)}
\]

\[
= (\cosh K_0)^{2N} (\cosh K_1)^{N} (\cosh K_2)^{N} 2^N \sum_{l,j,k} C_{ljk} w_0^{l-j-k} w_1^j w_2^k.
\tag{4.70}
\]

The last series summation is taken over all graphs with only two odd-degree vertices as well as with \( l - j - k \) NN \( xy \) bonds, \( j \) NN \( z \) bonds and \( k \) NNN \( z \) bonds (Fig. 4.5). The coefficient \( C_{ljk}(N, N^2, \ldots) \) is twice the number of such graphs for each \( l, j, k \), coming from the substitution \( \sum_{i \neq j} = 2 \sum_{i > j} \). Similarly,

\[
Q = (\cosh K_0)^{2N} (\cosh K_1)^{N} (\cosh K_2)^{N} 2^N [1 + \sum (\text{magnetic configurations})], \tag{4.71}
\]

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Figure 4.5: All types of magnetic configurations of the ANNNI model for $k = 1$, $j = 1$ and $l = 3$. Solid lines are NN bonds while dashed lines are NNN bonds. $B_{311} = 2 \times 48 = 96$.

but here the graphs are those with all vertices of even degree and thus vanish when considered together with the summation in Eq. 4.70. We therefore have

$$\chi_{\text{series}}(0) \equiv k_B T \chi = \sum_{l=0} \sum_{j+k \leq l} B_{ijk} w_{0}^{l-j-k} w_{1}^{j} w_{2}^{k}, \quad (4.72)$$

where $C_{ijk} = B_{ijk} N + D_{ijk} N^2 + \cdots$, i.e. $B_{ijk}$ is the coefficient linear in $N$ (Fig. 4.5).

Note that the case $k = 0$ ($k = j = 0$) reduces to the 3D (2D) Ising model.

To obtain the critical values at a certain $\kappa$, we need to expand the $q$-dependent susceptibility $\chi_{\text{series}}(q)$, similarly as Eq. 4.72 [3]

$$\chi_{\text{series}}(q) = 1 + 2 \sum_{n=1}^{11} \sum_{r+s \leq n} C_{nrs}(q) w_{0}^{n-r-s} w_{1}^{r} w_{2}^{s}, \quad (4.73)$$

where these coefficients were calculated by Ref [3].

\(^3\) In Ref [3], Oitmaa provided the coefficient in a data file, each line containing

```
counter n r s z 2C_{nrs}(z)
```

where $C_{nrs}(q) = C_{nrs}(z) \cos(2\pi q z)$.
4.5.3 Analysis of the ANNNI Series

For an arbitrary $q$, we sum over all lines and expand $\chi_{\text{series}}(q)$ in Taylor series of $\beta = 1/k_BT$ in Mathematica

$$\chi_{\text{series}}(q) = \sum_{n=0}^{11} a_n(q) \beta^n, \quad (4.74)$$

and

$$\frac{d \ln \chi_{\text{series}}(q)}{d\beta} = \sum_{n=0}^{10} b_n(q) \beta^n. \quad (4.75)$$

A Padé approximant of order $M$ and $N$ [161, 162]

$$\text{Padé}\left[\sum_{n=0}^{10} b_n(q) \beta^n; M, N\right] = \frac{F_M(\beta)}{G_N(\beta)}, \quad (4.76)$$

whose form assumes the existence of a singularity in the denominator, allows to estimate the location of the singularity. The closest real root of $G_N(\beta) = 0$ is used to estimate $\beta_c$ for a modulated phase with $q_c = q$.

For a given $\kappa$, we use above procedures at different $q$’s and get a set of $(q_c, \beta_c)$ pairs. The minimum of the curve fitting through these points on the $q$-$\beta$ plane is the real critical $q_c$ and $\beta_c$ for that $\kappa$.

To calculate the critical exponent $\gamma$, one defines

$$\gamma(\beta) \equiv (\beta_c - \beta) \frac{d \ln \chi_{\text{series}}(q_c)}{d\beta}, \quad (4.77)$$

and find the Padé approximant of $\gamma(\beta)$

$$\text{Padé}[\gamma(\beta); M, N] = \frac{P_M(\beta)}{Q_N(\beta)}, \quad (4.78)$$

The critical exponent in $\chi(q_c) \sim (\beta_c - \beta)^{-\gamma}$ ($T \to T_c^+$) is then estimated as [138]

$$\gamma = \frac{P_M(\beta_c)}{Q_N(\beta_c)}. \quad (4.79)$$
4.6 Cell Model of Cluster Crystals

In a crystal solid, a particle is essentially confined within a cell formed by its nearest neighbors and vibrates around its lattice site. The effective volume $v_f$ of the cell that can be explored by the particle is called its free volume [163, 164]. The entropy $S_f = N k_B \ln \frac{v_f}{\Lambda^3}$ associated with this local lattice vibration is the free volume entropy or vibrational entropy [128]. Because of the lack of translational movement, particles in solids lose the so-called communal entropy $S_c = N k_B$ of gaseous molecules. The free volume entropy therefore dominates in crystals and can be calculated with good accuracy at low temperatures or high pressures, that is when the lattice does not deform much from its regular shape. The cell model and free volume calculations have notably been applied to estimate the free energy of hard spheres [165, 166].

For the same reason, the cell model can be used to study the cluster crystal phases at low temperatures [17, 20, 77]. At low $T$ and high $\rho = N/V$, FCC cluster phases with occupancy $n_c$ and lattice constant

$$a = \left( \frac{\sqrt{2} n_c}{\rho} \right)^{1/3},$$

(4.80)

are formed. The cell confined by twelve nearest-neighbors in a FCC lattice, the Wigner cell, is a rhombic dodecahedron of height $h = a - \sigma$, where $\sigma$ is the radius of the exclusion sphere. Because the volume of a rhombic dodecahedron is $\frac{16}{3} \sqrt{3} s^3$, where $s = \frac{\sqrt{3}}{\sqrt{2}} h$ is its edge length, the free volume per lattice site is

$$v_f = 4\sqrt{2}(a - \sigma)^3.$$  

(4.81)

In each cell, the density is $\rho = n_c/v_f$ and the energy per particle is $\epsilon \frac{n_c(n_c-1)}{2} \frac{1}{n_c} = $
$\frac{\epsilon(n_c - 1)}{2}$ The free energy is thus

$$f(\rho, n_c) = k_B T \ln \frac{n_c \Lambda^3}{4\sqrt{2}(a - \sigma)^3} + \frac{\epsilon(n_c - 1)}{2}$$

$$= k_B T \ln \left[ \left( \frac{\sqrt{2} n_c}{\rho} \right)^{\frac{1}{3}} - \sigma \right] + \frac{\epsilon(n_c - 1)}{2} + f_0(T), \quad (4.82)$$

where $f_0(T)$ is a temperature-dependent constant and does not affect the determination of coexistence density at a fixed $T$. The common tangent of a series of free energy curves as a function of $1/\rho$ for different $n_c$'s identify the coexistence densities and pressures.

In singly occupied crystals, the exclusion sphere radius $\sigma$ is simply the hardcore diameter of particles. But in cluster crystals, $\sigma$ is roughly the diameter of the entire cluster on each site, which is not directly provided by the basic parameters of the system. By adjusting $\sigma (< a)$, one can shift the free energy curves along the $\rho$ axis until the resulting coexistence densities are consistent with the results obtained from other methods.
Before 1950, a group of renowned mathematicians and physicists including von Neumann, Ulam, Fermi, and Metropolis, had already been pioneering the numerical evaluation of integrals using random number sampling. Fermi was even said to perform the sampling with hand-operated machines already in the 1930s, back in Rome. But the computer implementation of these approaches was renamed by Metropolis with “Monte Carlo”, the name of the casino city in Monaco, in the spirit of its statistical sampling nature [167].

A significant breakthrough occurred in 1953, when the Tellers and the Rosenbluths joined the team at Los Alamos and invented the importance-sampling algorithm or Metropolis algorithm. The Monte Carlo method was then made applicable to a wide variety of problems, and notably to thermodynamic systems [168, 169].

In the 1970’s, Hastings generalized the Metropolis algorithm, reformulated it with the language of statistics, and brought it to the attention of the statistics community. The method was then referred to as the Metropolis-Hastings algorithm [170].

This chapter will review the basic conceptions and some technical details of the Monte Carlo method applied to molecular simulation. We will also introduce the
simulation methods that we developed to study modulated phases. With thermodynamic integration (TI), we can calculate the free energy of an arbitrary modulated phase, being stable or metastable. The $[N]pT$ ensemble simulations allow both particle number and volume to fluctuate, and thus dramatically accelerate the simulation procedure.

5.1 Monte Carlo Method

Consider the problem of evaluating the integral [171]

$$E[h(X)] = \int h(x)f(x)dx,$$

where $f(x)$ is a normalized function, i.e. $\int f(x)dx = 1$, and can be thought of as the probability density of a random variable $X$. A uniform sampling scheme generates $m$ sampling points $(X_1, X_2, ..., X_m)$ with density $f$ to evaluate the integral

$$\bar{h}_m = \frac{1}{m} \sum_{i=1}^{m} h(X_i) \to E[h(X)], \ \text{as } m \to \infty. \quad (5.2)$$

In practice, if the function $h(x)$ peaks around narrow ranges of values in space and is vanishingly small at most $x$ points, then the above estimation converges very slowly because most of the sampling is wasted at points that contribute very little to the integral. This problem is exactly what afflicts the evaluation of ensemble average of the potential energy,

$$\langle U \rangle = \frac{1}{Z} \int U(r^N)e^{-\beta U(r^N)}d\mathbf{r}^N, \quad (5.3)$$

in statistical mechanics. If we choose to generate sampling configurations $\mathbf{r}^N$ uniformly, i.e., to set $f(x) = 1$, then the function that needs to be calculated is $h(x) = U(r^N)e^{-\beta U(r^N)}$ in the numerator and $h(x) = e^{-\beta U(r^N)}$ in the denominator.
Z, which are both vanishingly small for most configurations. For this reason, uniform Monte Carlo sampling cannot reasonably be used to calculate thermal averages in statistical mechanics.

The central idea of importance sampling is to rewrite Eq. 5.1 as

\[ E[h(X)] = \int h(x) \frac{f(x)}{g(x)} g(x) dx, \quad (5.4) \]

to sample according to an alternative distribution \( g(x) \). Using this new sampling, the integral is estimated as

\[ \bar{h}_m = \frac{1}{m} \sum_{i=1}^{m} \frac{f(X_i)}{g(X_i)} h(X_i), \quad (5.5) \]

which converges much faster if \( g(x) \) is appropriately chosen. In order to evaluate \( \langle U \rangle \), if we choose \( g(x) = e^{-\beta U}/Z \), leaving \( f(x) = 1 \) and \( h(x) = U e^{-\beta U}/Z \), then

\[ U_m = \frac{1}{m} \sum_{i=1}^{m} \frac{1}{e^{-\beta U_i}/Z} U_i e^{-\beta U_i}/Z = \frac{1}{m} \sum_{i=1}^{m} U_i. \quad (5.6) \]

The function \( U_i \) has the advantage that it slowly varies over space.

The sampling distribution \( g(x) = e^{-\beta U}/Z \), however, is not known, because \( Z \) cannot be known in advance. To circumvent this problem, the Metropolis algorithm samples according to the relative probability \( e^{-\beta U} \) with a Markov chain, whose result is equivalent to that of sampling with the absolute probability \( e^{-\beta U}/Z \) [168].

5.2 Conventions on Reduced Units and Thermal Wavelength

To avoid numerical underflows/overflows, computer simulations rarely use SI units, which make the values of physical quantities differ from each other by orders of magnitude. In practice, it is convenient to express quantities in reduced units (Table 5.1). The original quantity \( A \) in SI unit can always be recovered from its dimensionless
Table 5.1: Reduced units.

<table>
<thead>
<tr>
<th>Quantity</th>
<th>Unit</th>
<th>Quantity in reduced unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Length</td>
<td>$\sigma$, hardcore diameter</td>
<td>$r^* = r/\sigma$, $\rho^* = \rho\sigma^3$</td>
</tr>
<tr>
<td>Energy</td>
<td>$\epsilon$, attraction well depth/repulsion barrier</td>
<td>$u^* = u/\epsilon$, $p^* = p\sigma^3/\epsilon$</td>
</tr>
<tr>
<td>Mass</td>
<td>$m$, mass of particles in the system</td>
<td></td>
</tr>
<tr>
<td>Temperature</td>
<td>$\epsilon/k_B$</td>
<td>$T^* = k_B T/\epsilon$</td>
</tr>
<tr>
<td>Time</td>
<td>$\epsilon/k_B \sigma \sqrt{m/\epsilon}$</td>
<td></td>
</tr>
</tbody>
</table>

reduced quantity $A^*$ if needed. To implement the reduced unit scheme in simulation, one just needs to set those units in Table 5.1, namely $\sigma$, $\epsilon$, $m$, $k_B$, to unity. Throughout this thesis, all quantities are studied in their reduced units. For convenience, we drop the superscript $^*$ in the rest of this work.

The reduced unit form of Planck’s constant $h$ is, however, inconvenient. By convention, one therefore sets $\Lambda = h/\sqrt{2\pi mk_B T} = 1$ in simulation as well. Under this convention,

$$\beta f^{id} = \ln(\rho) - 1,$$

$$\beta \mu^{id} = \ln(\rho),$$

$$\langle E \rangle = -\frac{\partial \ln Q}{\partial \beta} = -\frac{\partial \ln Z}{\partial \beta} = \langle U \rangle,$$

$$C_V = \left( \frac{\partial \langle U \rangle}{\partial T} \right)_V,$$

namely, the trivial kinetic energy background is neglected. Because $\Lambda = 1$ for all temperatures, the resulted $T$-$\rho$ phase diagram is rescaled along the $T$ axis compared to the one on a real scale $\Lambda$. But for a given temperature, this choice does not shift the phase boundaries in terms of the other thermodynamic variables.
5.3 Implementation

5.3.1 Periodic Boundary Condition

Although Monte Carlo simulations usually aim to study the thermodynamic properties of macroscopic systems, only a small number of particles ranging from $10^2 \sim 10^6$ can be dealt with in practice, due to the inherent finiteness of computer resources. For a cubic system of $10^3$ particles in 3D, a significant fraction of particles are located at the surface. In order to better characterize the bulk properties, periodic boundary conditions (PBC) are therefore used. Under PBC, the original simulation box corresponds to a primitive cell that is surrounded by an infinite number of replicated identical cells. All the cells form a periodic lattice and each particle in the simulation box interacts with particles not only in the primitive cell but also in all the other cells. When a particle in the simulation box moves, its images in all the other cells move accordingly. When a particle leaves the box, one of its image in a neighboring cell enters from the opposite side of the box (Fig. 5.1). Under PBC, every particle is treated as a bulk particle so surface effects are significantly reduced. The main problem of PBC is that correlations longer than the simulation box size $L$ are truncated. Also, only fluctuations that are compatible with $L$ are allowed. This feature is particularly important for the study of periodic microphases, whose accessible periodicities in a finite simulation box have to be commensurate with $L$.

5.3.2 Short-range Interactions: Minimum Image Convention, Cutoff and Tail Correction

Most interactions decay to zero asymptotically as the intermolecular distance $r$ approaches infinity. In 3D, interaction potentials $u(r)$ that decay faster than $r^{-3}$ are considered short-ranged because their volume integral converges. When particles interact via short-range interactions, the potential is usually truncated at a cutoff distance $r_{\text{cut}}$. In simulation, only interactions with $r < r_{\text{cut}}$ are calculated explicitly.
and beyond $r_{\text{cut}}$, $u(r)$ is treated in a mean-field way, which provide a tail correction to the total energy

$$U^{\text{tail}} = \frac{N\rho}{2} \int_{r_{\text{cut}}}^{\infty} u(r)4\pi r^2 dr.$$  \hspace{1cm} (5.11)

The cutoff $r_{\text{cut}}$ can be chosen to be arbitrarily large and to therefore include more particles at the expense of having simulations that take longer to run. The \textit{minimum image convention} adopts $r_{\text{cut}} \leq L/2$. In this case, a particle $i$ does not interact with all the images of another particle $j$. Among $j$ and all of its images, only the one that is at a distance $r$ smaller than $r_{\text{cut}}(\leq L/2)$ from $i$ is considered to interact with it (Fig. 5.1).

Although the truncation of $u(r)$ beyond $r_{\text{cut}}$ does not change most bulk properties in simulation, it can severely affect the location of the critical point, as demonstrated in the study of the Lennard-Jones fluid [172]. The tail of $u(r)$ is also very important.
at low temperatures where the strength of the interaction is effectively scaled up. Because of these possible drawbacks, finite-range interactions such as HS, PSM and SWL, are often preferred in simulations, because they strip away the effect of tail truncation.

5.3.3 Long-range Interactions: Ewald Summation

In contrast to short-range interactions, long-ranged interactions decay slower than $r^{-3}$, such as the Coulomb potential $u(r) \sim 1/r$. Because the integral calculating the tail energy diverges, one cannot simply truncate a long-range $u(r)$ at a $r_{cut}$ and treat the tail beyond $r_{cut}$ in a mean field way.

To calculate the Coulomb energy $U_{coul} = \frac{1}{2} \sum_{i \neq j} \frac{q_i q_j}{r_{ij}}$ between point charges $q_i$'s, for instance, the Ewald summation method is used [173]. The approach introduces a neutralizing screened charge (Gaussian charge distribution of standard deviation $\sqrt{2/\alpha^2}$) for each point charge. After being Fourier transformed, the original Coulomb potential $1/r$ is rearranged into the sum of a fast decaying real part $f(r)/r$ and a Fourier part $(1 - f(r))/r$ that is calculated in reciprocal space. The fast decaying function $f(r)$ turns out to be the error function complimentary $\text{erfc}(r) = \frac{2}{\sqrt{\pi}} \int_r^\infty \exp(-t^2)dt$.

In summary, the Coulomb energy in the Ewald sum is partitioned as [16]

$$U_{coul} = U_{\text{real}} + U_{\text{four}} + U_{\text{self}}. \tag{5.12}$$

The real part is

$$U_{\text{real}} = \frac{1}{2} \sum_{i \neq j}^N \frac{q_i q_j \text{erfc}(\alpha r_{ij})}{r_{ij}}, \tag{5.13}$$

where the parameter $\alpha$ determines the width of the Gaussian charge distribution and the decaying rate of the function $\text{erfc}(\alpha r)$. The Fourier part is summed in reciprocal
Figure 5.2: The dependence of the real and reciprocal space functions on the screening parameter $\alpha$, which needs to be optimized due to the tradeoff between the decaying rate of $\text{erfc}(\alpha r)$ and $\exp\left(-\frac{k^2}{4\alpha^2}\right)$.

space to guarantee convergence

$$U_{\text{four}} = \frac{1}{2} \frac{4\pi}{V} \sum_{k \neq 0} \frac{\exp\left(-\frac{k^2}{4\alpha^2}\right)}{k^2} |\rho(k)|^2,$$  \hspace{1cm} (5.14)

where

$$|\rho(k)|^2 = \sum_{i=1}^{N} q_i \exp(i k \cdot r_i) = \left| \sum_{i=1}^{N} q_i \cos(k \cdot r_i) \right|^2 + \left| \sum_{i=1}^{N} q_i \sin(k \cdot r_i) \right|^2. \hspace{1cm} (5.15)$$

Finally, because the sum of Gaussian function in real space includes the interaction of each Gaussian charge distribution with itself, a self-term needs to be subtracted

$$U_{\text{self}} = -\frac{\alpha}{\sqrt{\pi}} \sum_{i=1}^{N} q_i^2. \hspace{1cm} (5.16)$$

In a simulation of $N$ charges using $N_k$ wavevectors on a lattice, there are $N \times N$ cycles to the computation loop for the real part and $N \times N_k$ cycles for the Fourier part. By choosing an appropriate screening parameter $\alpha$ such that the $\text{erfc}(\alpha r_{ij})$ is dramatically decaying and essentially vanishes beyond a certain cutoff distance $r_{\text{cut}}$, one can reduce the number of cycles of the real part calculation by a factor of $2 \sim 4$ typically. In the optimal case, the scaling of the computational effort with system
size can be reduced from $O(N^2)$ to $O(N^{3/2})$ [16]. For example, in a cubic lattice of the size $L$, if $r_{\text{cut}} = \frac{L}{2}$ to adopt minimum image convention subject to periodic boundary condition, the number of cycles or pairs involved will be reduced from $N \times N$ to $N \times N/2$, i.e. interactions with charges in the corners of the simulation box will be neglected. However, to compensate, the $N_k$ in the Fourier part should be increased because $\exp\left(\frac{-k^2}{4\alpha^2}\right)$ then decays more slowly. The parameter $\alpha$ thus needs to be optimized to guarantee convergence of both series (Fig. 5.2).

Technically, it is worth noting that the sum over all wavevectors in the $k$-space can be simplified as a sum over only half of space, say those $k$’s to the right of and on the $k_x$-$k_z$ plane, and then multiplying by 2 (those $k$’s on the plane should be excluded to avoid double counting). The idea of summing over 1/8 of the wavevectors at one corner of the $k$-space and multiplying by 8 is not applicable in this case because of the asymmetry of cosine and sine functions.

It is also useful to note that, if dealing with a lattice system, $r_{ij}$, erfc($\alpha r_{ij}$) and the identities of all pair interacting charges $j$’s of each charge $i$ subject to $r_{ij} < r_{\text{cut}}$ can be stored in two-dimensional arrays once the lattice is generated. Similarly, $\rho(k)$ or $\cos(k \cdot r_i)$ and $\sin(k \cdot r_i)$ can be tabulated during the initialization of the simulation and updated by only adding the difference introduced at each simulation step.

5.3.4 Cell List

For finite-range interactions such as HS and fast decaying interactions such as the GEM-4, the cutoff $r_{\text{cut}}$ can be equal to or slightly larger than the particle soft/hard-core diameter $\sigma$, and thus much smaller than the box size, i.e. $r_{\text{cut}} \ll L/2$. A particle $i$ therefore only interacts with the small number of neighboring particles immediately surrounding it. However, the conventional energy algorithm requires one to check all the rest $N - 1$ particles in the simulation box to determine whether their distances to $i$ are smaller or larger than $r_{\text{cut}}$. This inefficient loop over all particles leads to
$N \times (N - 1)$ operations for each energy evaluation.

To improve the computation speed, the simulation box is usually divided into $N_{\text{cell}}$ small cells, where each has a side $r_{\text{cell}}$ slightly larger than $r_{\text{cut}}$, in the cell list method [174]. To identify particles interacting with a specific particle $i$, then one only needs to scan over the cell where $i$ is located and the nearest neighbor surrounding cells, which adds up to 27 cells in 3D. This approach is valid because $r_{\text{cell}} \geq r_{\text{cut}}$ and the 27 cells are guaranteed to contain all particles possibly interacting with $i$. In this method, there are $N \times 27 \times N/N_{\text{cell}}$ computations instead of $N \times (N - 1)$ for each energy evaluation. The cell list method is therefore much more efficient when the simulation box size is much larger than the cutoff such that $N_{\text{cell}} \gg 27$.

The data structure suitable for implementing the cell list is the (doubly) linked list [175]. In C, one can declare a structure `LinkedList` and use it to define a variable `CellTrack` as follows:
struct LinkedList {
    int WhichCell;
    int Prev;
    int Next;
};
struct LinkedList CellTrack[NumberOfParticles];

Here, CellTrack[i].WhichCell stores which cell particle i belongs to. All particles in the same cell are connected in a chain. CellTrack[i].Prev points to the previous particle identity and CellTrack[i].Next points to the next particle identity. When CellTrack[i].Prev = -1 (CellTrack[i].Next = -1), particle i is the first (last) one in the chain. To quickly pick up the first particle (head of the chain) in a given cell, we also need to define an array int HeadOfChain[NumberOfCells]. When HeadOfChain[j] = -1, cell j is empty. For instance, if particles 9, 2 and 6 are in cell 25 in order, then HeadOfChain[25] = 9 and

CellTrack[9].Prev = -1; CellTrack[2].Prev = 9; CellTrack[6].Prev = 2;
CellTrack[9].Next = 2; CellTrack[2].Next = 6; CellTrack[6].Next = -1.

At the beginning of the simulation, the cell list is first generated. Because Monte Carlo moves may displace particles out of their original cells, the cell list needs to be continuously updated during the simulation (Appendix D).

5.4 Monte Carlo Moves

To correctly reflect the equilibrium distribution, Monte Carlo moves from an old state o to a new state n are required to satisfy the detailed balance condition [16]

\[ \mathcal{N}(o)\alpha(o \rightarrow n)\text{acc}(o \rightarrow n) = \mathcal{N}(n)\alpha(n \rightarrow o)\text{acc}(n \rightarrow o), \]  

(5.17)

where \( \mathcal{N}(o) \) is the probability of being in the state o, namely, the Boltzmann distribution, \( \alpha(o \rightarrow n) \) is the probability of proposing the move and \( \text{acc}(o \rightarrow n) \) is the
probability of accepting the move. In simulations, the proposing step is often chosen
to be symmetric ($\alpha(o \rightarrow n) = \alpha(n \rightarrow o)$). From the partition functions, one can then
derive the acceptance ratio of basic Monte Carlo moves in various ensembles [16].

In the $NVT$ ensemble, the acceptance ratio of a translation of a randomly chosen
particle is

$$\text{acc}(N, V, E \rightarrow E + \Delta E) = \min \left\{ 1, e^{-\beta \Delta E} \right\}.$$  \hspace{1cm} (5.18)

In the $NpT$ ensemble, the acceptance ratio of a random compression/expansion of
the volume on a logarithmic scale is

$$\text{acc}(N, V \rightarrow V + \Delta V, E \rightarrow E + \Delta E) = \min \left\{ 1, e^{-\beta (\Delta E + p \Delta V) + (N + 1) \ln \frac{V + \Delta V}{V}} \right\}.$$  \hspace{1cm} (5.19)

In the $\mu VT$ ensemble, the acceptance ratio of a random insertion/removal ($+/-$) of
a particle is

$$\text{acc}(N \rightarrow N \pm 1, V, E \rightarrow E + \Delta E^{\pm}) = \min \left\{ 1, \eta^{\pm} e^{\pm \beta \mu - \beta \Delta E^{\pm}} \right\},$$  \hspace{1cm} (5.20)

where $\eta^{+} = V/(N + 1)$ and $\eta^{-} = N/V$. Note that $\Lambda$ has been set to unity in $\eta^{+}$ and $\eta^{-}$.

Although basic Monte Carlo moves are capable of sampling most simple phases,
under certain circumstances, their efficiency can be extremely low for reasons intrinsic
to the physics of the system such as a long correlation time or a correlation length.

5.4.1 Cluster Algorithms

We have already mentioned that, at the critical point, the system is characterized by
long a correlation length and strong fluctuations. In spin systems, a good simulation
close to the CP should generate a sequence of configurations that are very differ-
ent from one another, but the traditional single-spin flip algorithm takes a growing
number of steps to do so as one approaches the CP. To overcome the critical slowing
down, so-called cluster algorithms were invented, to study the Ising model [176, 177].
A cluster here is a collection of randomly connected spins. In simulation, a seed is initially chosen and the cluster is grown by randomly connecting neighboring spins with bonds to the seed or frontier edges, subject to specific probability laws. After the growth terminates, spins of the entire cluster are flipped.

The critical order-disorder transition of the ANNNI model also has the problem of critical slowing down, for which Pleimling has successfully developed a modified cluster algorithm [2]. The algorithm is described as follows

1. Randomly choose a core site $i$. Write $i$ in the cluster list and seed list.

2. For all the six nearest neighbors $j$ of $i$, and the two axial next-nearest neighbors $k$ of $i$, grow the cluster with the following strategy:
   (a) if $s_j = s_i$ and $j$ does not belong to the cluster yet, add $j$ to the cluster list and the seed list with probability $p_n = 1 - e^{-2\beta J}$;
   (b) if $s_k = -s_i$ and $k$ does not belong to the cluster yet, add $k$ to the cluster list and the seed list with probability $p_a = 1 - e^{-2\beta J\kappa}$.

3. Erase $i$ from the seed list.

4. Choose another seed site from the seed list.

5. Repeat 2–4 until the seed list is empty.

6. Flip the entire cluster with probability 1.

It can be shown that $p_n = 1 - e^{-2\beta J}$ and $p_a = 1 - e^{-2\beta J\kappa}$ satisfy the condition of microscopic reversibility (Appendix E).

5.4.2 Schultz-Kofke Volume Fluctuation

Traditional volume fluctuation sampling, in which the positions of all particles are affinely rescaled, is inefficient to simulate the PSM or any hardcore potentials at high density. Low temperature compressions of the PSM, like in a system of dense hard spheres, result in additional particle overlaps, whose cost is prohibitively high, and therefore are mostly rejected. To overcome this problem, we use an alternative
volume fluctuation algorithm recently developed by Schultz and Kofke [178], which improves the sampling efficiency by nearly three orders of magnitude at low temperatures in the PSM model. In the Schultz-Kofke algorithm, when volume changes from \( V \) to \( V + \Delta V \) on logarithmic scale, the position of each lattice site \( \mathbf{R}_i \) is first scaled affinely as \( \mathbf{R}_{i,\text{new}} = \mathbf{R}_{i,\text{old}} \left[ (V + \Delta V)/V \right]^{1/3} \), then the distance of each particle from its lattice site \( \mathbf{r}_j \) is changed as

\[
\mathbf{r}_{j,\text{new}} = \mathbf{r}_{j,\text{old}} \left( \frac{V}{V + \Delta V} e^{\beta(p\Delta V + \Delta E_{\text{lat}})} \right)^{1/(3N-3)}.
\]

(5.21)

The modified acceptance ratio is then

\[
\text{acc}(V \rightarrow V + \Delta V, E \rightarrow E + \Delta E) = \min \left\{ 1, e^{-\beta(\Delta E - \Delta E_{\text{lat}})} \right\},
\]

(5.22)

in which the effect of volume change is redistributed into the \( \mathbf{r}_j \) scaling step, and where \( \Delta E_{\text{lat}} \) is the change in lattice energy in the \( \mathbf{R}_i \) scaling step. The correct usage of this algorithm relies on conserving the crystal’s center of mass [178], for which one needs to be particularly careful in cluster crystals [179]. A possible solution is to track the shift in the center of mass using a Fourier transform of the configuration, as was done in the optimization of the order parameter in Sec. 4.1 [180]. Note that for step-wise discontinuous potentials like the PSM, \( \Delta E_{\text{lat}} \) is precisely zero if the particles sitting perfectly on lattice sites do not overlap before nor after a volume displacement. Yet if \( \Delta E_{\text{lat}} \) were nonzero, it would scale like \( N \), because all the particles on neighboring lattices would go from not overlapping to overlapping. Volume compressions with \( \Delta E_{\text{lat}} > 0 \) are thus rejected with overwhelmingly high probability at low temperatures.

5.5 Widom Insertion

It is sometimes useful to directly calculate the chemical potential \( \mu \), which corresponds to the free energy cost of inserting/removing a particle. For instance, one
way to identify the equilibrium occupancy $n_{eq}^c$ in cluster crystals is to calculate $\mu$ as a function of $n_c$ and locate $\mu_c = 0$ [15, 77, 179]. A elegant method for measuring $\mu$ in simulation is the particle insertion method, or the Widom insertion method [181].

In the constant $NVT$ ensemble,

$$\mu = \mu_{\text{id}}^{NVT} + \mu_{\text{ex}}^{NVT},$$

(5.23)

where the ideal part $\mu_{\text{id}}^{NVT} = k_B T \ln (\rho \Lambda^3)$ and the excess part $\mu_{\text{ex}}^{NVT}$ is evaluated by inserting a ghost particle repeatedly at a random position in the $N$-particle system [16]

$$\mu_{\text{ex}}^{NVT} = -k_B T \ln \left\langle \int d\mathbf{s}_{N+1} e^{-\beta \Delta U} \right\rangle_N.$$  

(5.24)

Two averages are taken in this integral. One is over configurations of the $N$-particle system in the ensemble, the other is over random positions of the ghost particle.

If interactions are truncated at a finite range, then the energy change can be divided into two terms $\Delta U = \Delta U^{\text{cut}} + \Delta U^{\text{tail}}$, with only the first term counted in Eq. 5.24. In this case,

$$\mu_{\text{ex}}^{NVT} = -k_B T \ln \left\langle \int d\mathbf{s}_{N+1} e^{-\beta \Delta U^{\text{cut}}} \right\rangle_N - k_B T \ln e^{-\beta \Delta U^{\text{tail}}}$$

$$= \mu_{\text{ex-\text{cut}}}^{\text{NVT}} + \mu^{\text{tail}},$$

(5.25)

where $\mu^{\text{tail}} = \Delta U^{\text{tail}}(N+1) - \Delta U^{\text{tail}}(N) = 2u^{\text{tail}}(\rho)$ [16].

Similarly, in the constant $NpT$ ensemble [16],

$$\mu = \mu_{\text{id}}^{\text{NpT}} + \mu_{\text{ex}}^{\text{NpT}},$$

(5.26)

with the ideal part

$$\mu_{\text{id}}^{\text{NpT}} = k_B T \ln (\beta p \Lambda^3) = k_B T \ln \langle \rho \rangle \Lambda^3 + k_B T \ln (\beta p / \langle \rho \rangle) = \mu_{\text{id}}^{\text{NVT}} + \mu_{\text{NpT-NVT}},$$

(5.27)
and the excess part

\[
\mu_{NP,T}^{ex} = -k_B T \ln \left( \frac{\beta p V}{N + 1} \int ds_{N+1} e^{-\beta \Delta U} \right)_N
\]

\[
= -k_B T \ln \left( \frac{\beta p V}{N + 1} \int ds_{N+1} e^{-\beta \Delta U^{cut}} \right)_N - k_B T \ln e^{-\beta \Delta U^{tail}}
\]

\[
= \mu_{NP,T}^{ex-cut} + \mu_{tail}
\]

\[
= -k_B T \ln \frac{\beta p (V)}{N + 1} + \mu_{NP,T}^{ex-cut} + \mu_{tail}
\]

\[
= - \mu_{NP,T-NVT} + \mu_{NP,T}^{ex}.
\]

To make the chemical potential obtained in NVT and NpT simulations consistent with the external \( \mu \) in the \( \mu VT \) simulation, one needs to be careful about tail corrections. The acceptance ratio of particle insertions/removals (+/−) is \( P \sim e^{±\beta \mu} \sim e^{±(\mu_{tail}-\Delta U^{tail})} \). Therefore, if \( \Delta U^{tail} \) is not considered in the energy difference of particle changes, the external chemical potential should be set to \( \mu - \mu_{tail} \).

5.5.1 Staged Widom Insertion

Despite its wide range of applications, the Widom insertion fails at low temperatures (large \( \beta \)) and high densities (large \( \Delta U \)), where the sampling function \( e^{-\beta \Delta U} \) can be vanishingly small. In the extreme case of hard sphere solids, almost no insertion can be accepted. The low temperature cluster crystal of the PSM behaves similarly to a hard sphere crystal. In order to calculate the chemical potential under this circumstance, the staged Widom insertion, which inserts the ghost particle in a sequence of steps, is therefore used [182, 183].

For penetrable spheres of diameter \( \sigma \) and repulsion barrier \( \epsilon \), we can choose \( M \) (\( M \sim 10 \)) steps indexed by \( i = 0, 1, 2, ..., M - 1 \), in which either \( \sigma \) or \( \epsilon \) is grown gradually. In the latter case, the \( i = 0 \) stage corresponds to a \( N \)-particle system and insertions of a ghost particle with repulsion barrier \( \epsilon/M \) are performed, resulting in
the chemical potential of the first stage $\mu^c_0$. The system at the $i = 1$ stage consists of $N$ real particles and one $\epsilon/M$ ghost particle. At $i = 1$, random insertions are replaced by random trials of growing the ghost particle barrier from $\epsilon/M$ to $2\epsilon/M$. This stage gives the intermediate chemical potential $\mu^c_1$. Stages with $i = 2, 3, ..., M - 1$ are analogous to $i = 1$. The total chemical potential is then estimated as the sum of these steps

$$\mu^c = \sum_{i=0}^{M-1} \mu^c_i.$$ (5.29)

5.6 Thermodynamic Integration

As for microphases and cluster crystals, knowledge of the free energy is often required to understand the phase stability and transitions. In contrast to thermal quantities such as energy and magnetization, which can be expressed as ensemble averages, free energies rely on information about the entire phase space and thus cannot be sampled with direct Monte Carlo simulations. Indirect techniques have thus been designed to calculate the free energies, among which thermodynamic integration (TI) is a standard approach.

The original idea of TI dates back to Kirkwood (1935), who proposed the coupling parameter formalism to study simple liquids [184]. A mathematically similar form was later developed in the so-called Hellmann-Feynman theorem (1939), where the average is taken over wave functions instead of over ensembles [185]. The TI method is also described as adiabatic switching in the context of molecular dynamics [135, 186].

In TI, one defines the coupled Hamiltonian $H_\lambda$ as a linear combination of the reference system $H_0$ and the system of interest $H_1$, for instance, as

$$H_\lambda = (1 - \lambda)H_0 + \lambda H_1.$$ (5.30)
where the coupling parameter $\lambda$ changes from 0 to 1 in most cases. However, the coupling range does not have to be designed within $[0, 1]$. In one of the earliest TI simulations, Frenkel and Ladd (1984) calculated the free energy of hard sphere solids by defining $H_\lambda = H_0 + H_1(\lambda)$, where 0 refers to the pure hard sphere system and 1 refers to the Einstein crystal with spring constant $\lambda$ [187] and so the parameter $\lambda$ changes from 0 to $\infty$ (or a very large $\lambda_{\text{max}}$, in practice).

For off-lattice particle systems, the Hamiltonian is often decomposed as $H_\lambda = K + U_\lambda$, with the kinetic part untouched by the coupling. In this case, the coupling is defined for the potential energy $U_\lambda = (1 - \lambda)U_0 + \lambda U_1$. (5.31)

For a system with an intermediate $\lambda \in [0, 1]$, the partition function is

$$Q_\lambda(N, V, T) = \frac{1}{\Lambda^N N!} Z_\lambda,$$

(5.32)

where the configuration integral is $Z_\lambda = \int d\mathbf{r}^N e^{-\beta U_\lambda}$, and the derivative of the Helmholtz free energy $F_\lambda = -k_B T \ln Q_\lambda$ with respect to $\lambda$ is

$$\left(\frac{\partial F_\lambda}{\partial \lambda}\right)_{N,V,T} = -\frac{1}{\beta} \frac{\partial \ln Q_\lambda(N, V, T)}{\partial \lambda} = -\frac{1}{\beta} \frac{\partial \ln Z_\lambda}{\partial \lambda} = -\frac{1}{\beta Z_\lambda} \frac{\partial Z_\lambda}{\partial \lambda}$$

$$= \int d\mathbf{r}^N \frac{\partial U_\lambda}{\partial \lambda} e^{-\beta U_\lambda} \frac{1}{Z_\lambda}$$

$$= \left\langle \frac{\partial U_\lambda}{\partial \lambda} \right\rangle_\lambda,$$

(5.33)

where $\left\langle \cdots \right\rangle_\lambda$ is the ensemble average evaluated for the system with $H_\lambda(U_\lambda)$. The difference in free energies between the two systems with $\lambda = 0$ and $\lambda = 1$ can be thus expressed as an integral

$$F_1 - F_0 = \int_{\lambda=0}^{\lambda=1} d\lambda \left\langle \frac{\partial U_\lambda}{\partial \lambda} \right\rangle_\lambda.$$
This method is valid if two requirements can be satisfied: 1. the reference point free energy $F_0$ can be solved analytically or at least numerically with high accuracy; 2. the integration path is smooth and reversible, i.e., no first-order transition nor hysteresis is involved, and the free energy of the system of interest $F_1$ can be obtained via Eq. 5.34.

To understand the necessity of the reversibility of the path, we consider the recently developed Jarzynski equality (2007), which relates the equilibrium free energy difference to the nonequilibrium work by

$$\Delta F = -\frac{1}{\beta} \ln \langle e^{-\beta W} \rangle.$$  \hspace{1cm} (5.35)

The work of a single trajectory

$$W = \int_0^{t_s} dt \lambda \frac{\partial H_\lambda}{\partial \lambda}$$  \hspace{1cm} (5.36)

is then performed on the system during the process of switching $\lambda$ from 0 to 1 over a time interval $t_s$ [188]. Only in the infinitely slow switching limit ($t_s \to \infty$), for which the process becomes reversible, does the Jarzynski equality reduce to the TI formula Eq. 5.34.

To establish a reversible integration path, the reference system and the system of interest clearly need to adopt the similar symmetry such that no first-order phase transition occurs along the path. For instance, while soft particles (PSM and GEM-n) can possibly use free particles as a reference system because they both allow particle overlap, particles with a hard core need to be integrated from a hard sphere system.

To calculate the integral from $\lambda = 0$ to $\lambda = 1$, one can use the Gauss-Lobatto quadrature (Appendix C). In this numerical integration scheme, certain specific $\lambda$’s (usually between 10 and 20 points) are chosen and the integral is expressed as the
weighted sum of the functions evaluated at those $\lambda$'s [189]. Although in general intermediate $\lambda$'s do not correspond to any physically relevant system, it is possible to relate them with systems at other temperatures by considering that the scaling of the potential energy $\beta(\lambda U_1)$ is actually applied over the temperature $(\beta\lambda)U_1 = \beta_\lambda U_1$ [190].

In principle, to study the free energy of a certain phase, one can explore the phase plane point by point using above TI method, each involving $\sim 20$ MC simulations. This approach is of course computationally expensive. To accelerate the calculation, whenever possible one therefore makes use of the fundamental thermodynamic relations, such as $\frac{\partial \beta f}{\partial \beta} = \frac{\langle U \rangle}{N}$ and $\frac{\partial f}{\partial \rho} = \frac{p}{\rho^2}$, to obtain free energies at neighboring temperatures and densities

$$\beta_2 f(\beta_2) = \beta_1 f(\beta_1) + \int_{\beta_1}^{\beta_2} \frac{\langle U \rangle}{N} d\beta,$$

$$f(\rho_2) = f(\rho_1) + \int_{\rho_1}^{\rho_2} \frac{p}{\rho^2} d\rho.$$  

(5.37)  

(5.38)

5.6.1 TI of ANNNI and IC

The Hamiltonian for the system of interest is $H_1 = H_{\text{ANNNI}}$ or $H_1 = H_{\text{IC}}$ in this case. For the lamellar phases observed on lattices with $N = L_x L_y L_z$ sites, we propose a reference that has decoupled spins under a $z$-axial periodically oscillating field $B(z)$ with amplitude $B_0$

$$H_0 = -B_0 \sum_{i=1}^{N} s_i B(z_i).$$

(5.39)

It trivially follows that in a system with fluctuating magnetization

$$\frac{F_0}{NT} = -\frac{1}{L_z} \sum_{z=1}^{L_z} \ln \left[ 2 \cosh \left( \frac{B_0 B(z)}{T} \right) \right].$$

(5.40)
The amplitude $B_0$ should be sufficiently strong to prevent layer melting and changes of layer periodicity as the field is turned off, yet sufficiently weak to allow sampling of the integrand\(^1\). Fortunately, the relatively high free-energy barriers between neighboring modulated phases make phase transitions along the integration path highly unlikely, even if sections of the path are formally metastable. Due to the broken symmetry between the different coordinate axis, we can also, without loss of generality, lock the lamellae in a specific orientation when initializing configurations for the IC model.

The applied field $B(z)$ needs not be the exact equilibrium profile of the modulated layers as long as the integration from $B(z)$ can be done reversibly. For instance, either square or sinusoidal fields can be used as reference states for the study of modulated phases with integer periodicity. The free energy results of both approaches agree with high accuracy (Fig. 5.4). The equivalence also holds in the low-temperature regime, where the ground state profile is more akin to a square well than to a pure sine function [5]. Because sinusoidal fields are “soft” in the interlayer region, which helps averaging the layer fluctuations, and because they provide a compact and efficient way to describe non-integer periodic lamellae, we choose

$$B(z) = \sin(2\pi q z + \phi_0), \quad (5.41)$$

where a small phase angle $\phi_0$ is added to prevent the lattice planes from directly overlapping with zeros of the field.

The IC model, which must remain charge neutral, requires that the reference partition function $Z_0$ be computed subject to a fixed magnetization constraint. In the infinite system limit this correction is negligible, but on a finite lattice it may affect transition temperatures. For the paramagnetic phase, the reference system

\(^1\) For the paramagnetic phase, where formally $B_0 = 0$, the integration is equivalently taken from finite $T$ to infinity.
Hamiltonian $H_0$ with $B_0 = 0$ results in $F_0/N = -T \ln 2$ for an unconstrained system (Eq. 5.40), but the properly constrained reference system instead has

$$\frac{F_0'}{NT} = -\frac{1}{N} \ln \left( \frac{N}{N/2} \right),$$

(5.42)

where $\binom{N}{N/2}$ is the binomial coefficient. For $N = 12^2 \times 24 = 3456$ spins, the difference between the two results is $\sim 0.001T$, which may be significant because of the small entropy differences between layered phases. Calculating $F_0'$ is not, however, as straightforward for $B_0 \neq 0$. One has to define a thermodynamic integration path between fluctuating and constant magnetization systems

$$H_\lambda = H_0 + \lambda \left| \sum_i s_i \right|,$$

(5.43)

with $\lambda$ going from 0 to $\infty$. In practice, $\langle \frac{\partial H_\lambda}{\partial \lambda} \rangle = |\sum_i s_i|$ rapidly decays to zero with growing $\lambda$, and therefore integrating to a finite $\lambda$ of order unity is sufficient. The zero-magnetization free energy $F_0'$ is then obtained by adding the correction from thermodynamic integration to $F_0$ from Eq. 5.40 (Fig. 5.4). We note, however, that even in the small IC systems studied here, the free energy corrections for different modulated phases are very similar for a given temperature. Phase transitions are thus only imperceptibly affected by the shift.

Investigating the $T$-frustration plane point by point is computationally wasteful. Data acquisition is significantly accelerated by thermally integrating to nearby temperatures $T_1$ or frustrations $\kappa_1$ (or, equivalently, $Q_1$) using a known state point $(T_0, \kappa_0)$ as reference by

$$\frac{F_1(T_1, \kappa_0)}{T_1} - \frac{F_1(T_0, \kappa_0)}{T_0} = \int_{T_0}^{T_1} \left( \frac{\partial F_1}{\partial 1/T} \right)_{\kappa_0} d(1/T)$$

(5.44)

or

$$F_1(T_0, \kappa_1) - F_1(T_0, \kappa_0) = \int_{\kappa_0}^{\kappa_1} \left( \frac{\partial F_1}{\partial \kappa} \right)_{T_0} d\kappa,$$

(5.45)
Figure 5.4: (top left) Thermodynamic integration of the ANNNI model at $\kappa = 0.7$ and $T = 2.5$ for phase $\langle 2 \rangle$ using sinusoidal and square fields as reference. (bottom left) Change in the structure factor peak height along the integration path and the free energy results for the two different references. (top right) Thermodynamic integration of the IC model at $Q = 0.8$ and $T = 1.06$ for phase $\langle 21^4 \rangle$. The integration curve from a fluctuating to a constant magnetization system is shown in the inset. (bottom right) The structure factor at different wavevectors demonstrates the preservation of the modulation along the integration path.

where

$$\left( \frac{\partial F_1}{\partial 1/T} \right)_{\kappa_0} = \langle H_1 \rangle_{\kappa_0} \quad (5.46)$$

and

$$\left( \frac{\partial F_1}{\partial \kappa} \right)_{T_0} = \left\langle \frac{\partial H_1}{\partial \kappa} \right\rangle_{T_0} = \left\langle J \sum_{[i,j]_z} s_i s_j \right\rangle_{T_0}. \quad (5.47)$$

In practice, the free energy results are fitted with a polynomial of degree three or four. The free energy at any point within a relatively short interval is then interpolated from the parameterized function.

5.6.2 TI of SWL

Because of the existence of a hard core in the model, the SWL cannot be integrated directly from the free particles. Instead, we use hard spheres under modulated field...
as the reference system. But the partition function and $F_0(\rho)$ of this system at a nonzero density $\rho$ are not easily solved, especially when the field function is nontrivial. We thus perform a second integration from free particles under field to hard spheres under field, which is equivalent to integrating the reference system from zero density to $\rho$. Because the system of free particles under field is solvable, $F_0(\rho)$ can then be obtained from this integration over density.

In this section, we discuss the TI of SWL in three steps: the solution of systems of free particles under field, the integration from free particles under field to hard spheres under field, and the integration from hard spheres under field to SWL.

**Solution of Free Particles (Ideal Gas) under Field**

In general, the potential of free particles under field is defined as

$$U(r^N) = -\sum_{i=1}^{N} B(r_i),$$

which tends to trap particles in the positive-field part of space.

**a. Lamellar Phases**

For lamellar phases, the field is discussed in two cases: step Haar function field and sinusoidal field.

The Haar function field is defined as,

$$B(r) = \begin{cases} B_0, & z \in \bigcup_{n=0}^{n=m-1} \left[\frac{2n}{2m}, \frac{(2n+1)}{2m}\right] \\ -B_0, & z \in \bigcup_{n=0}^{n=m-1} \left[\frac{(2n+1)}{2m}, \frac{(2n+2)}{2m}\right] \end{cases}$$

where $m$ is the number of periods over the length $L_z$ and $n = 0, 1, ..., m - 1$. The configuration integral and free energy using this field are therefore

$$Z = V^N \cosh^N(\beta B_0),$$

and

$$f_0^{ex} = -k_B T \log \cosh(\beta B_0).$$
The sinusoidal field is defined as

\[ B(\mathbf{r}) = B(z) = B_0 \cos(kz) \]  \hspace{1cm} (5.52)

where the wave vector \( k = 2\pi n/L_z \) has \( n \) complete oscillatory periods in the box. It can be shown that

\[ Z = V^N I_0^N (\beta B_0), \]  \hspace{1cm} (5.53)

and

\[ f_0^{\text{ex}} = -k_B T \ln I_0(\beta B_0), \]  \hspace{1cm} (5.54)

where \( I_0(x) \) is the modified Bessel function of the first kind, which for integer \( n \) is

\[ I_n(x) = \frac{1}{\pi} \int_0^\pi e^{x \cos \theta} \cos(n \theta) d\theta. \]  \hspace{1cm} (5.55)

b. Cylindrical Phases

For cylindrical phases we use a 2D modulated field defined as

\[ B(\mathbf{r}) = B(x, y) = B_0 \cos(kx) \cos \left( k \left( \frac{x}{2} + \frac{\sqrt{3} y}{2} \right) \right) \cos \left( k \left( \frac{x}{2} - \frac{\sqrt{3} y}{2} \right) \right), \]  \hspace{1cm} (5.56)

where \( k = 2\pi n/L_x \) is the wave vector with integer \( n \). The lattice constant between domains of cylinders is \( a = L_x/\sqrt{3} \). The simulation box can then be chosen with \( L_y = ma = m \sqrt{3} n L_x \) for integer \( m \) to meet with periodic boundary conditions. The free energy using this field is

\[ f_0^{\text{ex}} = -k_B T \ln I, \]  \hspace{1cm} (5.57)

where the integral \( I = \frac{1}{L_x L_y} \int_0^{L_x} \int_0^{L_y} e^{\beta B(x, y)} dx dy \) is evaluated numerically.
Integration One: From Free Particles under Field \((\rho = 0)\) to Hard Spheres under Field

To calculate the free energy \(f_{\text{HSF}}(\rho)\) of hard spheres under field (HSF) at density \(\rho\), we integrate from zero density \([16]\)

\[
 f_{\text{HSF}}(\rho) - f_{\text{id}}(\rho) = f_{\text{HSF}}(0) - f_{\text{id}}(0) + \int_0^\rho \frac{p(\rho') - \rho'k_B T}{\rho'^2} d\rho',
\]

(5.58)

where the ideal gas part \(f_{\text{id}}(\rho) = k_B T \ln(\rho \Lambda^3) - 1\). The HSF at zero density (ideal gas under field) therefore has

\[
 f_{\text{HSF}}(0) - f_{\text{id}}(0) = f_0^{\text{ex}},
\]

(5.59)

where \(f_0^{\text{ex}}\) has been discussed above.

To evaluate the integral \(\int_0^\rho \frac{p(\rho') - \rho'k_B T}{\rho'^2} d\rho'\) numerically, one can in principle do a series of \(NVT\) simulations at various densities \(\rho\) and calculate the corresponding pressure \(p(\rho)\) using virial relations. But if particles have potentials with singularities and discontinuities like the SWL, or if particles with a polydisperse size distribution are present, \(p\) is not easily calculated in simulation. We instead perform a series of \(NpT\) simulations at various \(p\) and get corresponding \(\langle \rho \rangle\) to calculate the integral.
To preserve the modulation periodicity, special care needs to be taken over the volume fluctuations in the $NpT$ simulation of hard spheres under field. If the field is fixed and box size fluctuates under the pressure, two problems may arise. First, dissipative work is done when the particles are driven by the changes of the box with respect to the field. Second, the field becomes incommensurate with the box length under the periodic boundary condition. The field therefore has to be attached to the box and changed affinely with it. However, then another problem occurs in simulation when 1D modulation (lamellae) and 2D modulation (cylinders) are studied. Such systems can be mechanically unstable in which the stress distribution is not spatially homogenous. For instance, in the hard sphere lamellar system with periodicity along $z$ axis, empty space between layers has little stress such that spacing between layers shrinks and layers grow in $xy$ directions under compression. To overcome this problem, we attach an artificial spring to the two ends of the box in the $z$ direction. This spring introduces a harmonic potential $U_s = k_s(L_z - L_{z0})^2$ with spring stiffness $k_s$. The response of the box under pressure along the $z$ axis is then governed by the spring and can be made to fluctuate around the required length $L_{z0}$.

Note that the spring does not intervene during the following integration from hard spheres under field to SWL, because the volume is fixed and therefore $U_s = 0$.

**Integration Two: From Hard Spheres under Field to SWL**

The above calculations provide us the free energy of the reference system $f_{HSF}(\rho)$, from which we perform a TI with a coupled potential

$$U_\lambda(r^N) = -(1 - \lambda) \sum_{i=1}^{N} B(r_i) + \sum_{i>j} u_{HS}(r_{ij}) + \lambda \sum_{i>j} u_{AR}(r_{ij}).$$

(5.60)

We have here divided the SWL potential $u_{SWL}$ into a sum of a hardcore potential $u_{HS}$ and a attraction-repulsion part $u_{AR}$. The ensemble average that needs to be
evaluated is then
\[
\frac{\partial U_\lambda}{\partial \lambda} = \sum_{i=1}^{N} B(r_i) + \sum_{i>j} u_{AR}(r_{ij}).
\] (5.61)

**Free Energy Minimization**

In order to identify the equilibrium modulated phase at a phase point, we need to calculate the free energy for various morphology and wave number \(q = n/L\). In the minimization with respect to \(q\), we can tune not only the number of periods \(n\) but also the simulation box size \(L\), such that \(q\) changes continuously.

5.6.3 TI of PSM and GEM-4

For the cluster crystal, the potential energy of the coupled system with particles at \(r^N = \{r_1, r_2, \cdots, r_N\}\) is defined as in Ref. [77, 179]

\[
U_\lambda = (1 - \lambda)U_0(r^N) + \lambda U(r^N),
\] (5.62)

where

\[
U(r^N) = \sum_{i=1}^{N-1} \sum_{j>i}^N u(r_{ij}),
\] (5.63)

and the coupling parameter \(\lambda\) varies from 0 to 1. We choose the reference system to be free particles under spherically attractive potential wells centered at the lattice sites

\[
U_0(r^N) = \sum_{i=1}^{N} u_0(r_i),
\] (5.64)

with

\[
u_0(r) = \begin{cases} 
\epsilon_0 & r \in \bigcup_{i=1}^{N} v_0(R_i) \\
0 & \text{otherwise}
\end{cases}
\] (5.65)
where $v_0(R_i)$ is the size of one attractive spherical well at lattice vector $R_i$. The free energy of the reference system at temperature $T$ is therefore [179]

$$
\beta f_0 = \ln \frac{N}{(V - V_0) + V_0 e^{-\beta \epsilon_0}} - 1,
$$
(5.66)

where $V_0 = N_c v_0$ is the total volume of the potential wells. The parameters $v_0$ and $\epsilon_0$ are tuned for each simulation to obtain enough fluctuations and a smooth integration path. The constrained free energy of the solid phase with a certain occupancy is then

$$
f_c = f_0 + \int_0^1 \frac{N}{N} \left\langle U - U_0 \right\rangle \lambda d\lambda,
$$
(5.67)

as illustrated in Fig. 5.6 [179]. The integration path is continuous and shows no hysteresis, as the preservation of crystal symmetry in Fig. 5.6 also illustrates. For fixed $\rho, T, N_c$, free energy integrations are performed for various $N$’s until the equilibrium $n_c^{eq}$ is identified from Eq. 3.9 [19].
5.7 \([N]pT\) Ensemble Simulation

Traditional simulation methods either fix the number of particles, as in constant \(NVT\) or \(NpT\) simulations, or the lattice spacing, as in constant \(\mu VT\) simulations, which in all cases prevent cluster crystals from relaxing to their equilibrium \(n_c\). An ensemble that would allow both \(N\) and \(V\) to fluctuate may naively seem to resolve the problem, but such \(\mu pT\) ensemble would have unbounded fluctuations, as discussed in Chapter 3. Earlier simulation approaches thus employed elaborate free energy schemes in order to minimize \(f_c\) and \(g_c\) [19] or equivalently to locate \(\mu_c = 0\) [15, 77]. In these schemes, locating the equilibrium structure requires tens of free energy calculations, each necessitating one to two dozens of independently sampled state points. This high computational cost limits the method’s applicability to all but the simplest models. In order to reduce the computational burden and broaden the range of accessible models one should limit resorting to free energy integrations. We present below such an approach based on reformulating the expanded isothermal-isobaric \([N]pT\) ensemble [191].

5.7.1 \([N]pT\) Ensemble

An \([N]pT\) ensemble differs from the generalized ensemble (Sec. 3.7) by constraining \(N\) within bounds \([N_{\text{min}}, N_{\text{max}}]\) that (if properly chosen) enclose \(n_c^{\text{eq}}\) at the studied \(p\), \(T\), and \(N_c\). The new partition function

\[
\Upsilon^* = \sum_{N=N_{\text{min}}}^{N_{\text{max}}} e^{\beta \tilde{G}_N} \sum_V e^{-\beta p V} \sum_E \Omega(N, V, E) e^{-\beta E},
\]

has weights \(\tilde{G}_N \equiv \tilde{g}_N N\) that are both explicit (extensive) and implicit functions of \(N\) to control the probability of visiting states of varying \(N\). These weights are not known \textit{a priori}, but can be self-consistently determined, as is done for the multicanonical ensemble [192], the expanded ensemble parallel tempering [193], and Wang-Landau
sampling [194, 195]. Once the weights are determined, the joint probability of observing a state with a specific $N$, $V$, and $E$ is

$$\mathcal{P}(N, V, E) = \frac{1}{\Gamma^*} \Omega(N, V, E) e^{\beta \tilde{G}_N - \beta p V - \beta E},$$

and the marginal probabilities of observing a state with specific $N$ and $V$ or with a specific $N$ only are, respectively,

$$\mathcal{P}_{NV}(N, V) = \sum_E \mathcal{P}(N, V, E) \sim e^{\beta \tilde{G}_N - \beta p V} Q(N, V, T)$$

$$\mathcal{P}_N(N) = \sum_E \sum_V \mathcal{P}(N, V, E) \sim e^{\beta \tilde{G}_N} \Delta(N, p, T).$$

### 5.7.2 Simulation Method

During a simulation, in addition to standard particle and logarithmic volume displacements [16], particle insertions (+) and removals (−) are used with the acceptance ratio

$$\text{acc}(N \rightarrow N \pm 1, V, E \rightarrow E + \Delta E^\pm) = \min \left\{ 1, \eta^\pm e^{\beta \Delta G^\pm - \beta \Delta E^\pm} \right\},$$

where $\Delta G^\pm = \tilde{G}_{N \pm 1} - \tilde{G}_N$, $\eta^+ = V/(N + 1)$, $\eta^- = N/V$, and $\Delta E^\pm$ is the energy cost of inserting/removing a particle. The validity of this algorithm is demonstrated in Appendix F.

In order to self-consistently determine $\tilde{G}_N$, for each iteration $i$ we obtain a histogram $\mathcal{W}^i(N, V, E)$ that keeps track of the frequency at which each $(N, V, E)$ state is observed. After $i$ iterations, the normalized histogram gives the probability of observing a state

$$\mathcal{P}^i(N, V, E) = \frac{\mathcal{W}^i(N, V, E)}{\sum_{N,V,E} \mathcal{W}^i(N, V, E)}$$

that approximates the density of state

$$\Omega^i(N, V, E) = \mathcal{P}^i(N, V, E) e^{-\beta \tilde{G}^i_N - \beta p V - \beta E}$$

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and the other partition functions

\[ Q^i(N, V, T) = \sum_E \Omega^i(N, V, E) e^{-\beta E} \quad \text{and} \quad (5.74) \]

\[ \Delta^i(N, p, T) = \sum_V Q^i(N, V, T) e^{-\beta p V}. \quad (5.75) \]

Note, however, that even once the scheme has converged \( \Omega, Q \) and \( \Delta \) all lack a multiplicative constant \( \Upsilon^* \), so the conjugate field that is used for the \((i+1)\)th iteration

\[ \beta \tilde{G}^{i+1}_N = -\ln \Delta^i(N, p, T) \quad (5.76) \]

also lacks an additive constant \( \tilde{C}^i \). The iterative procedure is repeated until the marginal distribution \( \mathcal{P}_N(N) \) is flat within \([N_{\text{min}}, N_{\text{max}}]\), i.e., \( e^{\beta \tilde{G}_N} \Delta(N, p, T) = \text{constant} \) (Eq. 5.70), which coincides with the convergence criterion \( \tilde{G}^{i+1}_N = \tilde{G}^i_N + \tilde{C}^i \) for all \( N \in [N_{\text{min}}, N_{\text{max}}] \) (Appendix F).

A final simulation using the converged weights constructs the equilibrium \( \mathcal{W}(N, V, E) \).

This last \([N]pT\) simulation is conceptually equivalent to running a series of \( NpT \) simulations with different \( N \)'s, where the transition probability of hopping from one to the other is governed by \( \tilde{G}_N \). The weights thus capture the constrained Gibbs free energy \( G_c \) of the system up to a constant \( C \). Because the equilibrium occupancy is determined by minimizing \( g_c \) with respect to \( N \) (Eq. 3.9), the unknown constant \( C \), which leads to a \( C/N \) term, must be obtained by thermodynamic integration at a given \( N_0 \in [N_{\text{min}}, N_{\text{max}}] \).

5.8 Histogram Reweighting

Because \([N]pT\) ensemble simulations rely on building the full density of state, histogram reweighting provides the thermodynamic properties of the system at neighboring \( T \) and \( p \) [196]. The implementation of histogram reweighting often uses a logarithmic summation scale to avoid overflow/underflow in large systems [196] (Appendix G).
5.8.1 Reweighting Over Pressure

Histogram reweighting over pressure, for instance, provides $B_{\text{vir}}$ and $(\frac{\partial n_{eq}}{\partial p})_T$ from a single $[N]pT$ simulation. For each $N$ within the bounds, the volume $V$ is sampled with the conditional probability, knowing $N$, at pressure $p$

\[ P_{V|N}(V|N) = \frac{P_{N}(N)}{P_N(N)} = \frac{e^{-\beta p V} Q(N,V,T)}{\Delta(N,p,T)}. \]  

(5.77)

The thermal average of $M$ configurations obtained from Monte Carlo sampling at pressure $p$ is thus

\[ \langle V \rangle = \frac{\sum_V V P_{V|N}^{-1} e^{-\beta p V} Q}{\sum_V P_{V|N}^{-1} e^{-\beta p V} Q} = \frac{\sum_V V}{M}. \]  

(5.78)

Now, suppose the simulation is run at a nearby different pressure $p_0$. The probability of observing a state becomes

\[ P_{V|N,0}(V|N) = \frac{e^{-\beta p_0 V} Q(N,V,T)}{\Delta(N,p_0,T)}. \]  

(5.79)

In order to evaluate the same average quantity $\langle V \rangle$ at $p$, while sampling configurations at $p_0$ subject to the distribution $P_{V|N,0}$, the histogram is reweighted

\[ \langle V \rangle = \frac{\sum_V V P_{V|N,0}^{-1} e^{-\beta p V} Q}{\sum_V P_{V|N,0}^{-1} e^{-\beta p V} Q} = \frac{\sum_V V e^{-\beta(p-p_0)V}}{\sum_V e^{-\beta(p-p_0)V}}. \]  

(5.80)

For each $n_c$, i.e., for each $N$ at fixed $N_c$, this reweighting scheme provides $\langle v \rangle = \langle V \rangle/N$ over a short pressure interval enclosing $p_0$. By integrating $\langle v \rangle$ for each $n_c$, the constrained Gibbs free energy per particle over a pressure interval follows

\[ g_c(p, n_c) - g_c(p_0, n_c) = \int_{p_0}^{p} \langle v \rangle dp'. \]  

(5.81)
For each neighboring pressure $p$, $g_c(p, n_c)$ is minimal at the equilibrium occupancy $n_c^{eq}$ and the equilibrium Gibbs free energy per particle $g(p)$. The corresponding equilibrium Helmholtz free energy per particle $f_c(p) = g_c(p) - p\langle v \rangle$ is similarly available for neighboring densities. Numerically, the volume for each $N$ obtained from $[N]pT$ simulations is reweighted at neighboring pressures and then fitted to a third-order polynomial in pressure, before using Eq. 5.81. Figure 5.7 shows an example of the resulting $g_c(p, n_c)$. As a rule of thumb, histogram reweighting is sufficiently accurate as long as $N^{eq}$ remains within the bounds $[N_{min}, N_{max}]$.

5.8.2 Reweighting Over Temperature

Histogram reweighting over temperature similarly provides $\alpha_{vir}$ and $\left(\frac{\partial n_c^{eq}}{\partial T}\right)_p$ from a single $[N]pT$ simulation. One can show that the thermal average of the volume at neighboring temperatures can be calculated from the configurations sampled at $T_0$

$$
\langle V \rangle = \frac{\sum_V V e^{-(\beta-\beta_0)pV} \sum_E \Omega(N, V, E)e^{-(\beta-\beta_0)E}}{\sum_V e^{-(\beta-\beta_0)pV} \sum_E \Omega(N, V, E)e^{-(\beta-\beta_0)E}}.
$$

(5.82)

To calculate the Gibbs free energy at fixed $p$ and neighboring $T$, one reweights the isobaric-isothermal partition function. Although the real partition function differs
from the sampling result by a multiplicative constant $C^*$, this constant is determined
by the free energy at $T_0$ by

$$
\beta_0 G_c(N,p,T_0) = -(\ln \Delta(N,p,T_0) + \ln C^*).
$$

(5.83)

In a Monte Carlo scheme, the fraction phase space sampled $\Delta(N,p,T_0)$ is propor-
tional to the number of accepted configurations $M$, because these configurations are
already Boltzmann weighted. Note that in this formulation, $C^*$ absorbs the normal-
ization by the total number of the samples considered. For instance, if the algorithm
is ran twice as long, $C^*$ is halved. The sampling partition function at neighboring
temperatures is thus

$$
\Delta(N,p,T) = \sum_V e^{-(\beta-\beta_0)pV} \sum_E \Omega(N,V,E)e^{-(\beta-\beta_0)E},
$$

(5.84)

and the corresponding constrained Gibbs free energy for each $N$ is

$$
\beta G_c(N,p,T) = -(\ln \Delta(N,p,T) + \ln C^*).
$$

(5.85)

Sample reweighting results are shown in Fig. 5.7.

5.8.3 Reweighting in the ANNNI Model Near $T_c$

In order to accurately calculate the critical properties of the ANNNI model, we
also use histogram reweighting over temperature near $T_c$, which allows us to sample
temperatures at various orders of magnitude of proximity to the transition, as is
needed for finite-size scaling analysis. The calculation of all the quantities needed,
including $\langle m(q) \rangle$, $\chi(q)$, and $C_V$, reduces to the estimation of ensemble averages
such as $\langle m(q) \rangle$, $\langle m(q)^2 \rangle$, $\langle E \rangle$, and $\langle E^2 \rangle$. We therefore perform simulations at a
temperature $T_0$ close to $T_c$ and obtain the histogram $\mathcal{W}(E,m(q))$ over energy $E$ and
magnetization $m(q)$. The ensemble averages at neighboring temperatures are then
simply
\[
\langle E(T) \rangle = \frac{\sum E e^{-(\beta - \beta_0)E}}{\sum E e^{-(\beta - \beta_0)E}}.
\] (5.86)

5.9 Finite-size Scaling and Critical Exponent

Theoretically, the singularity of thermal functions can be observed at phase transitions, such as the jump in specific volume in a first-order transition or the divergence of susceptibility in a second-order transition. But this is only true in the thermodynamic limit. Strictly speaking, there is no phase transitions in a finite system at non-zero temperature [141]. All simulations can only be for finite systems. To extract the information about the phase transition, finite-size scaling techniques are often used [196–198]. In this section, we discuss the finite-size scaling of the critical order-disorder transition in the ANNNI model and the critical isostructural transition in the GEM-4 model.

5.9.1 ANNNI Order-Disorder Transition

Among the order parameters introduced in Sec. 4.1, the generalized magnetization decays \( \langle m(q) \rangle \sim (T_c - T)^\beta \) with critical exponent \( \beta \), but its decay properties are not ideal for numerically detecting critical temperatures in finite systems. The monotonically increasing \( S(q) \) is, however, ill-suited for detecting the paramagnetic-modulated transition in simulations, because, like \( \langle m(q) \rangle \), it does not give a clear numerical signature of \( T_c \). The generalized susceptibility

\[
T\chi(q) \equiv \frac{1}{N}\langle \tilde{s}_q \tilde{s}_{-q} \rangle - \langle \tilde{s}_q \rangle \langle \tilde{s}_{-q} \rangle = N\langle m^2(q) \rangle - N\langle m(q) \rangle^2,
\] (5.87)

i.e., the second cumulant of the magnetization, is, however, quite efficient to detect phase transitions. It indeed diverges on both sides of the transition \( \chi(q_c) \sim |T - T_c|^{-\gamma} \) with critical exponent \( \gamma \), as would \( \chi(0) \) in the Ising model (Fig. 5.9). But directly
correcting for finite-size effects results in a high-sensitivity of the transition location
to simulation noise. The Binder cumulant route is more convenient for detecting \( T_c \),
because its value at the critical point \( U_4^* \) is straightforwardly insensitive to scaling
the system size [66, 199]. For layered phases, a generalization of the expression

\[
U_4(q) = 1 - \frac{\langle m^4(q) \rangle}{3\langle m^2(q) \rangle^2}
\]  
(5.88)

in terms of the second and the fourth \( \langle m^4(q) \rangle = \langle \tilde{s}_{q}^2 \tilde{s}_{-q}^2 \rangle / N^4 \) q-modulated magnetization moments is needed.

Because of the anisotropy of the modulated phases, it is useful to review how
breaking spatial isotropy may affect critical properties. In a system of dimensions
parallel \( L_{\parallel} \equiv L_z \) and perpendicular \( L_{\perp} \equiv L_x = L_y \) to the modulation propagation,
the correlation length \( \xi \) may diverge with different critical exponents

\[
\xi_{\parallel} \sim |T - T_c|^{-\nu_{\parallel}}, \quad \xi_{\perp} \sim |T - T_c|^{-\nu_{\perp}}.
\]  
(5.89)

The critical Binder cumulant \( U_4^* = U_4(q_c, T_c) \) is then invariant for a fixed ratio
\( L_{\parallel} / L_{\perp}^{\nu_{\parallel}/\nu_{\perp}} \) (Fig. 5.8) [200]. At a uniaxial Lifshitz point, such as in the ANNNI
model [2], \( \nu_{\parallel} \simeq \frac{1}{2} \nu_{\perp} \) [47, 89]. For the PM transition, at \( \kappa > \kappa_L \), we also consider
the possibility of anisotropic critical behavior. Although a direct determination of
\( \nu_{\parallel} / \nu_{\perp} \) is numerically difficult, indirect finite-size study of systems with a fixed ratio
\( L_{\parallel} / L_{\perp} = 2 \) shows that \( U_4^* \) does not vary at the PM transition (Fig. 5.8). This
observation suggests that \( \nu_{\parallel} / \nu_{\perp} \approx 1 \), i.e., \( \xi_{\parallel} \) and \( \xi_{\perp} \) diverge with the same critical
exponent \( \nu_{\parallel} = \nu_{\perp} \equiv \nu \) at the PM transition. Critical anisotropy is thus neglected here.

Binder cumulants also allow to independently determine the critical exponent \( \nu \)

\(^2\) For isotropic critical points, the universality of \( U_4^* \) reduces to the aspect ratio of the system, as expected.
Figure 5.8: Binder cumulant of the ANNNI model at $\kappa = 0.8$ and $q_c = 0.2$. The curves, which intersect at the critical temperature $T_c = 4.141$, monotonically decrease with $T$. The limited validity regime of histogram reweighing results is here responsible for the non-monotonicity. (Inset) Finite-size scaling analysis of the peak of the derivative of $U_4(q_c)$ and $\ln\langle m(q_c)^2 \rangle$. The logarithm scales as $1/\nu$, which here gives $\nu = 0.66(2)$.

using the peak value of the derivative of $U_4$

$$\ln \left( \frac{\partial U_4}{\partial 1/T} \right)_{\text{max}} = \frac{1}{\nu} \ln L + \text{constant.} \quad (5.90)$$

A similar relation for the structure factor gives [66, 201]

$$\ln \left( \frac{\partial \ln \langle m^2(q) \rangle}{\partial 1/T} \right)_{\text{max}} = \frac{1}{\nu} \ln L + \text{constant.} \quad (5.91)$$

The system size $L$ in the scaling relation can be either $L_\parallel$ or $L_\perp$ as long as the ratio $L_\parallel/L_\perp$ is fixed. For an isotropic critical point, as long as the dimensions are rescaled by the same factor, the form of the collapse and the critical exponents remain unchanged (Fig. 5.8).

Once $\nu$ and $T_c$ are obtained, the critical exponents $\beta$ and $\gamma$ can more easily be determined through finite-size scaling [66]. The quantities $L^{\beta/\nu}\langle m(q_c) \rangle$ and $L^{-\gamma/\nu}\chi(q_c)$
Figure 5.9: Finite-size scaling of the magnetization (top), susceptibility (middle) and heat capacity (bottom) of the ANNNI model at $\kappa = 0.8$ and $q_c = 0.2$, using $\nu = 0.66$, $\gamma = 1.32$, $\beta = 0.34$, $\alpha = -0.01$, and $C_c^\infty = 20$.

Overlap for different system sizes when drawn as a function of the scaled temperature $L^{1/\nu}(T - T_c)/T_c$. The heat capacity can also be similarly rescaled, but only if $C$ diverges at $T_c$, as at transitions with Ising universality. For a transition with XY-universality, for which $\alpha = -0.01$, $C$ peaks at a finite value $C_c^\infty$ in the infinite system size limit. The proper scaling relation is then $L^{-\alpha/\nu}(C - C_c^\infty)$ [202, 203]. But such rescaling for a small $\alpha$ is subject to sizable numerical errors [202]. The hyperscaling relation $2 - \alpha = 3\nu$ is used instead to determine $\alpha$ [146].
5.9.2 GEM-4 Isostructural Transition

Simulation techniques for first-order transitions are fairly straightforward [204]. The accurate determination of the critical point, however, involves a renormalization group based finite-size scaling [205]. At the apparent critical temperature $T_c(L)$ of a finite system of linear size $L$, the distribution of the order parameter adopts a universal form, once properly rescaled, which allows to extrapolate $T_c$. In the liquid-vapor transition, the distribution $\mathcal{P}_L(M)$ of the linearly transformed$^3$ density operator $M = \frac{\rho - su}{1 - sr}$ with parameters $s$ and $r$ at $T_c(L)$, where $u$ is the energy density, collapses onto the double-peaked Ising universality distribution $\mathcal{P}(x)$ [18, 205, 206], with scaling variable $x \sim L^{\beta/\nu}(M - M_c)$. After $T_c(L)$ and $\rho_c(L)$ have been determined for various system sizes, the infinite-system critical temperature and density can then be extracted from the scaling relationships

$$T_c(L) - T_c(\infty) \sim L^{-(\theta+1)/\nu}$$
$$\rho_c(L) - \rho_c(\infty) \sim L^{-(1-\alpha)/\nu},$$

(5.92)

where for the Ising universality $\theta = 0.54$, $\alpha = 0.11$ and $\nu = 0.629$ [204]. In order to locate the isostructural critical point in the GEM-4, we use the similar idea, i.e., by calculating the distribution $\mathcal{P}(\rho)$ of the order parameter $\rho$ at the apparent critical temperature.

The $[N]pT$ ensemble method conveniently locates the coexistence densities at a pair of coexistence temperature and pressure from the two minima of the calculated $g_c$ curve. The two minimum wells should be of equal depth, indicating an equal chemical potential for the two phases. By histogram reweighting over temperatures and pressures, we can extrapolate coexistence densities at neighboring phase points. 

To calculate $\mathcal{P}(\rho)$ from our knowledge of $G_c = g_c N$, we first reexamine the statistical

$^3$ Due to the lack of particle-hole symmetry observed in the Ising model, the liquid-vapor first-order coexistence density curve is asymmetric. A linear transform of the density $\rho$ is needed to compare with the symmetric Ising magnetization [205].
The mechanics of cluster crystals.

At given \( N, p \) and \( T \), the constrained Gibbs free energy \( G_c(N_c) = G_c(N, p, T, N_c) \) as a function of \( N_c \) can be considered as a Landau free energy with order parameter \( N_c \),

\[
e^{-\beta G_c(N_c)} = \sum_{\nu} e^{-\beta G_{\nu}} \delta(N_c - N_{\nu}^c),
\]

(5.93)

where \( \sum_{\nu} \) means sum over all states indexed by \( \nu \) subject to the constant \( NpT \) constraint and the delta function \( \delta(N_c - N_{\nu}^c) \) is 1 when \( N_c = N_{\nu}^c \) and zero otherwise. The equilibrium Gibbs free energy \( G(N, p, T) \) therefore satisfies

\[
e^{-\beta G} = \sum_{N_c} e^{-\beta G_c(N_c)} \simeq e^{-\beta G_c(N_{eq}^c)},
\]

(5.94)

where the last approximation states that the term with equilibrium \( N_{eq}^c \) dominates the sum. Analogously, we can define the Landau free energy \( G_V(V) \) and \( \tilde{G}(N_c, V) \) as

\[
e^{-\beta G_V(V)} = \sum_{\nu} e^{-\beta G_{\nu}} \delta(V - V_\nu),
\]

(5.95)

and

\[
e^{-\beta \tilde{G}(N_c, V)} = \sum_{\nu} e^{-\beta G_{\nu}} \delta(N_c - N_{\nu}^c) \delta(V - V_\nu),
\]

(5.96)

which are related by

\[
e^{-\beta G_V(V)} = \sum_{N_c} e^{-\beta \tilde{G}(N_c, V)} \simeq e^{-\beta \tilde{G}(N_{V}^c, V)}.
\]

(5.97)

Again, for a given volume \( V \), there exists a specific \( N_{eq}^V \) such that the term \( e^{-\beta \tilde{G}(N_{eq}^V, V)} \) dominates the sum over \( N_c \). At the apparent critical temperature and pressure of a \( N \)-particle system, the density fluctuations result from fluctuations of both \( V \) and \( N_c \). Because one specific \( N_{eq}^V \) dominates for each \( V \), we can consider that the
density fluctuations are along the \( N_c = N_c^V \) contour of the two-dimensional \( \tilde{G}(N_c, V) \) surface. In other words, the density fluctuation is governed by the Landau free energy \( G_V(V) \simeq \tilde{G}(N_c^V, V) \) for fixed \( N \), namely, the distribution \( \mathcal{P}(\rho) \sim e^{-\beta G_V(\frac{N}{\rho})} \).

In \([N]pT\) ensemble simulations, \( N_c \) is fixed while \( N \) fluctuates. The distribution of density is then governed by the Landau free energy \( \tilde{G}(N_0(\rho), \rho) \), where \( N_0 \) is the most probable particle number for a given density \( \rho \). We can show that in the \([N]pT\) ensemble, if densities are binned under the definition \( \rho = N/\langle V \rangle \) for each \( N \in [N_{\text{min}}, N_{\text{max}}] \), then \( N \) is approximately equal to \( N_0 \) for that density. The conditional probability of observing a particle number \( N \) given the density \( \rho \), \( \mathcal{P}(N|\rho) \sim \mathcal{P}(N, \rho) \sim N \mathcal{P}_{NV}(N, V) \), where the joint distribution

\[
P_{NV}(N, V) \sim e^{\beta G_c(N,p,T,N_c)} e^{-\beta p V} e^{-\beta F_c(N,V,T,N_c)}.
\]

If we consider the \([N]pT\) ensemble simulation to be a series of \( NpT \) simulations, then for each \( N \), there exists an average volume \( \langle V \rangle \). We can thus formally write
\[
P_{NV}(N, V) \sim \frac{e^{-\beta(p V + F_c(N,V,T,N_c))}}{e^{-\beta G_c(N,p,T,N_c)}} = \frac{e^{-\beta \tilde{G}(N_c, V)}}{e^{-\beta \tilde{G}(N_c, \langle V \rangle)}}.
\]

If \( V \) is extremely narrowly distributed around \( \langle V \rangle \), then deviations of the particle number from its most probably value is vanishingly small. Because the distribution is narrow, the factor \( N \) in front of \( P_{NV}(N, V) \) does not affect the peak position of \( \mathcal{P}(N|\rho) \) and the most probable particle number is approximately \( N = \rho \langle V \rangle \). This result can be verified from simulation by comparing the mostly sampled \( N_0 \) for a given density \( \rho = N/V \) and the particle number under the definition \( N = \rho \langle V \rangle \) (Fig. 5.10). We can therefore use the Landau free energy \( \tilde{G}(N, \rho = N/\langle V \rangle) = G_c(N = \rho \langle V \rangle, p, T, N_c) \) to analyze the density fluctuations.

Another challenge with \([N]pT\) simulations is that both particle number and volume are allowed to fluctuate, which results in the trivial exponentially growing probability in the distribution \( \mathcal{P}(\rho = N/\langle V \rangle) \sim e^{-\beta G_c(N = \rho \langle V \rangle, p, T, N_c)} \), due to the increasing number of states with \( N \). Although \( g_c = G_c/N \) shows a double well, \( G_c \) mainly
increases linearly with $N$, and the wells are invisible on the overall scale. We can correct this exponential growth by normalizing the distribution with $e^{-\beta \mu^{eq} N}$, where $\mu^{eq}$ is the minimum of $g_c$ and also the coexistence chemical potential.

In summary, for a given system size $L$, the distribution of density $\mathcal{P}_L(\rho = N/(V)) \sim e^{\beta(\mu^{eq} N - G_c)}$, where $G_c = g_c N$ is the converged field in the $[N]pT$ simulation. The linear size $L$ is defined as $V^{1/d}$ and $N^{1/d}$ in constant $\mu VT$ and $NpT$ simulation respectively [207]. But in the $[N]pT$ simulation, neither $N$ nor $V$ are fixed. We thus tentatively use $L \propto N_c^{1/d}$ as the linear system size.

5.10 Shearing under Lees-Edwards Boundary Condition

We use the algorithm in Ref. [208] to shear the ANNNI system, which forms lamellae perpendicular to the $z$ axis, in the $y$ direction with rate $\dot{\gamma} = M_s p_s$ (Fig. 5.11). In each MC cycle, after $N$ MC steps are performed, we carry out $M_s L_z$ attempts to shear the system by one lattice site with probability $p_s$ as

(1) Generate a random number $0 \leq r \leq 1$.

---

4 The arbitrary constant $C$ has been subtracted using one thermodynamic integration.
Figure 5.11: Left: shearing of the ANNNI system in $y$ direction with rate $\dot{\gamma}$. Right: comparison of the periodic boundary condition (PBC) with the Lees-Edwards boundary condition (LEBC) under shear. Three simulation boxes are packed vertically. Each one is akin to the red “Z”-shape box, the top of which has been sheared to the right by a distance $dL$. The interaction range within the cutoff distance is represented by the circles. Identities of particles across the top and bottom boundaries (shaded) are wrongly captured by the PBC. In the LEBC, particles above the top boundary are shifted to the right by $dL$ while particles below the bottom boundary are shifted in the opposite direction.

(2) If $r \leq p_s$, choose a random layer $z_0$ out of $L_z$. For all lattice sites with $z \geq z_0$, shift the lattice by $y_i \rightarrow y_i + 1$.

Periodic boundary conditions are used in the $x$ and $y$ directions, while the Lees-Edwards boundary conditions is necessary in the $z$ direction [209] (Fig. 5.11).
6

Results of the ANNNI and IC Models

In this chapter, we present the simulation results of the two microphase-forming spin models, the ANNNI and the IC model. Equilibrium modulated phases are obtained from thermodynamic integration. The critical properties and roughening transition of the ANNNI model are also reported.

6.1 Simulation Details

We perform constant $T$ Monte Carlo (MC) simulations on a cubic lattice under periodic boundary conditions, using $N = L_x L_y L_z = 40^2 \times 240$ spins for the ANNNI model and $N = 12^2 \times 24$ spins for the IC model, unless otherwise noted. Ewald summation (Sec. 5.3.3) is used to compute the long-range Coulomb interactions in the IC model [16, 173]. The phases studied have wave numbers $q = n/L_z$ with integer $n$’s, which keeps modulations commensurate with the lattice. We initialize the modulated phases with a sinusoidally varying spatial probability of the desired periodicity. We find that the system relaxes to the equilibrium spin profile for a


given \( xy \) plane

\[
    s_{xy}(z) \equiv \frac{1}{L_x L_y} \sum_{i \in xy} \langle s_i \rangle
\]  

(6.1)

irrespectively of the initialization scheme as long as it has the correct periodicity.

Basic MC sampling consists of single-spin flips for the ANNNI model. Spin exchanges that enforce charge neutrality, are used for the IC model. Phase-space exploration gains in efficiency by complementing the basic sampling with iterations that take advantage of phase symmetry.

- For the modulated phases, layer swaps allow for the individual layer thickness to fluctuate while preserving the overall periodicity. Multiple layer swaps are necessary to alter the periodicity and therefore even neighboring modulated phases are well separated in configuration space.

- Near the (paramagnetic-modulated) PM transition, an anisotropic cluster algorithm for the ANNNI model [2] and a modified Wolff algorithm that considers the corrections from long-range interaction for the IC model [6] are used, in order to capture the strong fluctuations (Sec. 5.4.1).

- For systems with an applied external magnetic field, random displacements of the entire modulated pattern relative to the field along the \( z \) axis help sample the translational degrees of freedom.

For reference point integrations, up to \( 10^5 \) MC moves (\( N \) attempted spin flips or exchanges per move) are performed after \( 5 \times 10^4 \) MC moves of preliminary equilibration. For the thermal and frustration integrations, only \( 10^4 \) MC moves are necessary, because the free energy is not as sensitive to the accuracy of the integration slope as it is to its starting point over the small \( T \) intervals considered. In the vicinity of the critical transitions, we also use the multiple histogram algorithm, in order to obtain
high precision results with a minimal amount of computations [201] (Sec. 5.8). Our implementation uses a logarithmic summation scale, in order to avoid sum overflow in large systems [196].

Figure 6.1: (a) Energy and free energy results for the ANNNI model at $\kappa = 0.7$ for modulations ranging from phase $\langle 2 \rangle$ to phase $\langle 2^93^14^1 \rangle$ at melting. The PM transition $T_c = 3.988$ (vertical dashed line) is obtained from $U_4^*$. (b) Under the same conditions as (a), equilibrium devil’s staircase compared with the rescaled soliton result (dashed line), and $\langle m(q) \rangle$ compared with the power-law decay form with $\beta = 0.34$ obtained from finite-size scaling (solid line). Note that in the low-temperature limit, the square profile of phase $\langle 2 \rangle$ gives $\langle m(q) \rangle \to 2^{-1/2}$. (c) Energy and free energy results for the IC model at $Q = 0.8$ for phases $\langle 1 \rangle$, $\langle 21^4 \rangle$ and $\langle 21^2 \rangle$, and the paramagnetic phase. The PM transition $T_c = 1.15(1)$ is obtained from $C$. The short vertical dashed line indicates the transition temperature between phases $\langle 1 \rangle$ and $\langle 21^2 \rangle$, obtained from simple annealing (see text) [6]. (d) Under the same conditions as (c), devil’s staircase and normalized structure factor. Note that in the low-temperature limit, the profile of phase $\langle 1 \rangle$ gives $\sqrt{\langle m(q) \rangle^2} \to 1$. 

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6.2 Phase Transitions between Layered Phases

The size of the energy gap between neighboring phases with $q$'s commensurate with the simulation box reflects the limited and constrained choice of modulations realizable on a finite periodic lattice (Fig. 6.1). In an infinite periodic system, where all rational modulations are valid but irrational $q$'s are excluded, this gap would be infinitely small because rational numbers are dense on the real axis [59, 93, 210]. The smooth and extended energy curves for the different modulations are also characteristic of strongly metastable phases (Figs. 6.1 and 6.2). The high free-energy barriers between layers of differing periodicity result in phases that are sufficiently long-lived to persist throughout the entire simulation if the $L_x L_y$ cross-section is large enough. Different phases can be observed at a given temperature and frustration, depending on how the system is initialized. For smaller cross sections, however, the reduced number of spins involved in changing the periodicity lowers these transition barriers.
For a fixed system size, although a longer $L_z$ allows the study of more modulated phases, the need to keep these phases stable limits the maximal aspect ratio $L_{\parallel} : L_{\perp}$ of the simulation lattice. In practice, the selected ratio must balance these competing demands. A microscopic understanding of the transition mechanism between layered phases of different periodicity is still incomplete [5], but we empirically find that a size ratio of 2:1 is sufficient.

The crossing of the free-energy curves for neighboring modulated phases identifies the transition temperature. Using this approach side steps the hysteresis that otherwise afflicts annealing-based methods and results in a more accurate depiction of the modulated regime than had previously been obtained [6, 92, 93, 211]. For the IC model, for instance, the free energy calculations locate the phase transitions at temperatures at least 10% lower than reported in Ref. [6], where the system was prepared in the $T = 0$ ground state and studied by simulated annealing. At $Q = 0.8$, we can even identify a commensurate modulated phase $\langle 21^4 \rangle$ that was entirely missed by the annealing study. The other possibly missed commensurate phase $\langle 21^{10} \rangle$ is, however, unstable here as well, presumably because of finite size effects (Fig. 6.1). Qualitatively similar results are also obtained for $Q = 0.144$ and $Q = 0.17$ (not shown).

By integrating over frustration at low temperature we can also identify the boundary between phases of integer periodicity in the IC model. The results at finite temperatures agree very closely with the $T = 0$ energy derived transitions. The location of the free energy cross over between phases $\langle 1 \rangle$ and $\langle 2 \rangle$ (not shown) as well as between phases $\langle 2 \rangle$ and $\langle 3 \rangle$ is only mildly affected by temperature (Fig. 6.2). The thermal fluctuations produce a similar free energy shift of both phases, which leaves the $Q$ location of the transition unchanged. We expect similar results at other $\langle n \rangle$-$\langle n + 1 \rangle$ phase transitions.

The PM transition is not accurately obtained by direct free energy comparisons
for either systems. For the ANNNI model, the continuous transition is best studied through the specialized tools of critical phenomena (Sec. 5.9). But even for the IC model, the fluctuation-induced first-order transition does not result in sufficiently high free energy barriers for noticeably supercooling the paramagnetic phase in such a small system. The system instead rapidly freezes into a modulated phase below the transition and shows only a minimum of hysteresis. As a result, the transition identified from the heat capacity peak by annealing in Ref. [6] is equivalent to what is obtained here. A more careful system size dependence study would be necessary to refine the transition estimate.

6.3 Devil’s Staircase and Order Parameter

The equilibrium wave number obtained from the free energy results displays the characteristic devil’s staircase [99]. The stability regime of a given modulated phase stretches over an ever smaller $T$ range upon cooling. For the ANNNI model, the predicted truncation of the sequence before reaching the antiphase makes the staircase “harmless” [212], but the simulated system size is here insufficient to distinguish this scenario from the infinite “devil’s last step” sequence in which no commensurate phase is missed [59, 212]. The overall shape of the decay can, however, be compared with the soliton theory prediction [99]. Though the soliton does not correctly capture the PM transition temperature, once $T$ is linearly rescaled to make $T_c$ coincide, the agreement is fairly good (Fig. 6.1).

The equilibrium generalized magnetization behaves similarly to its $q = 0$ version in the Ising model. For the ANNNI model around $T_c$, the quantity grows monotonically upon cooling. It continuously increases at first, but jumps discontinuously upon reaching the antiphase. In this last region the magnetization profile tends toward a periodic square, whose profile structure is only partially captured by a simple sinusoidal function. For the IC model, the renormalized structure factor, which is
indistinguishable from $\langle m(q) \rangle$ at low temperatures, is also not an ideal order parameter (Sec. 4.1). When the system changes from phase $\langle 21^2 \rangle$ to $\langle 21^4 \rangle$, for instance, the peak height actually goes down. Here again, the modulation profile is not well captured by a simple sinusoidal function. In both models, the inclusion of higher order harmonics might better detect growing order upon cooling.

6.4 Modulation at Melting

The periodicity of the modulated phase at the PM transition $q_c(\kappa)$ (or $q_c(Q)$) is remarkably insensitive to the theoretical approach used for capturing its behavior. In the ANNNI model, the agreement between simulation results, mean-field theory [13], HT series expansion [3, 10], and the critical scaling near the Lifshitz point

$$q_c \sim |\kappa - \kappa_L|^{\beta_l},$$

(6.2)

using either the critical exponent from series expansion $\beta_l = 0.5 \pm 0.05$ [3, 10] or from renormalization group $\beta_l = 0.514$ [213], is very good (Fig. 6.3). The similarity of the

![Simulation wave number periodicity at melting $q_c$ for different frustration strengths of the ANNNI (left) and the IC (right) models superimposed with theoretical predictions. The solid line for the IC model captures the accessible wave number for $L_z = 24$. (left inset) The critical exponent $\gamma$ obtained by finite-size scaling is compared with the high-temperature series expansion [3], and the field-theory predictions for the exponent [8, 9]. The Lifshitz information is taken from Ref. [2].](image-url)
RG critical exponent with the mean-field value further suggests that the dependence of microphase periodicity on frustration is much easier to capture than the transition temperature. The free energy correction due to fluctuations is likely similar for neighboring layered phases.

For the IC model, the mean-field prediction for the continuously changing $q_c$ is also within the simulation accuracy in the layered regime (Fig. 6.3), but the relatively small lattice size prevents a quantitative assessment of the theoretical predictions. In the high $Q$ regime, where a Néel-paramagnetic-modulated phase triple point is expected, our coarse simulation estimate $Q_N \approx 15.8$ clearly differs from the mean-field prediction of 11.5 [7]. A large deviation between the theoretical prediction and the direct calculation is also observed at $T = 0$, where $Q_{N}^{0} = 9.549$ and 15.33, respectively [7]. Both those differences can mostly, and possibly completely, be explained by the low accuracy of the lattice Fourier transform in the large $Q$ limit, where modulated phases of small domains form [7]. Note, however, that the critical nature of the $Q_N$ point, which depends on the properties of the modulated-Néel transition, could also impact its location. If it is a bicritical point, fluctuations could result in larger deviations from the mean-field predictions. A generalization of the free energy simulation approach to other modulated geometries should be able to resolve this question, but is beyond the scope of this work.

6.5 ANNNI Critical Behavior

The critical properties of the ANNNI model have been extensively studied using a high-temperature (HT) series expansion [3, 10, 96]. For instance, critical temperatures can be estimated by resumming truncated series with Padé approximants [3, 159]. The arbitrariness of selecting the Padé order results in a range of estimates (Tables 6.1 and 6.2). The values of $T_c$ obtained from finite-size scaling quantitatively agree with these estimates and are an order of magnitude more precise than both
the HT series results and previous simulation estimates [1, 4].

The critical exponents from the HT series expansion, however, only qualitatively agree with the simulation results. Finite HT series with coefficients that changes continuously with $\kappa$ can only smoothly approximate dramatic changes in critical behavior, but the critical exponents change discontinuously on both side of the Lifshitz point. The apparent continuous variation of $\gamma$ with $\kappa$ obtained from HT series expansion is thus unphysical and should disappear if an infinite number of terms in expansion were used [10]. Field theory arguments suggest, however, that the critical exponents should have Ising universality below the Lifshitz point, XY above the Lifshitz point [8], and uniaxial Lifshitz universality at the Lifshitz point [89]. The Ising [1] and Lifshitz point [2] predictions have been previously confirmed by Monte Carlo simulations, but above the Lifshitz point the model’s behavior is not so clear.

In particular, the HT series results for $\gamma$ at large $\kappa$ undershoot the XY exponent value. In the words of Ref. [3], at high $\kappa$ “a puzzling and unexplained feature [of the HT series expansion results] is the apparent decrease of $\gamma$ to something like the Ising value.” Later similar studies did not quite resolve this question, and even suggested that a different type of universality might be observed beyond $\kappa \approx 2$ [96]. The critical exponent results support a XY universality of the transition for all $\kappa > \kappa_L$ studied. The values of $\nu$ and $\gamma$ agree with each other and with the XY values, and are often significantly different from the Ising exponents, despite the relatively large error bars (Table 6.2 and Fig. 6.3). The finite-size scaling of $C$ using $\alpha$ derived from hyperscaling relations further supports the agreement (Fig. 5.9). These observations, however, shed some doubt on the validity of the predicted transition at $\kappa \approx 2$ [96].

The XY universality of the PM transition can be understood from the similarity between its two-component order parameter and that of the XY model [215, 216]. A mean-field picture for the order parameter of the ANNNI model (Eq. 4.14) suggests that a spin $i$ in the modulated phase can be thought of evolving within a magneti-
Table 6.1: Critical parameters of the ANNNI model for $\kappa \leq \kappa_L = 0.270(4)$ obtained by finite-size scaling of cubic systems with $L = 16, 32, 40, 64, 80$ for $\kappa = 0.1$ and 0.2 and from previous simulations [1, 2]. Ising values are given for reference. The uncertainty on $T_c$ and $q_c$ from the HT series expansion results from the Padé approximant method [3]. At $\kappa_L, \nu_\parallel$ is reported. The starred $^\ast \alpha$ results are obtained from the hyperscaling relation $3\nu = 2 - \alpha$ (or $\alpha + 2\beta + \gamma = 2$ for $\kappa = 0.24$).

<table>
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<tr>
<td>$T_{c}^{MC}$</td>
<td>4.512</td>
<td>4.265(1)</td>
<td>4.15(2)</td>
<td>3.987(1)</td>
<td>3.86(2)</td>
<td>3.77(2)</td>
<td>3.7475(5)</td>
</tr>
<tr>
<td>$T_{c}^{HT}$</td>
<td>4.51(2)</td>
<td>4.26(2)</td>
<td>4.13(2)</td>
<td>3.98(2)</td>
<td>3.85(2)</td>
<td>3.76(2)</td>
<td>3.75(2)</td>
</tr>
<tr>
<td>$\nu$</td>
<td>0.63</td>
<td>0.62(1)</td>
<td>0.61(3)</td>
<td>0.62(2)</td>
<td>–</td>
<td>0.51(4)</td>
<td>0.33(3) [1]</td>
</tr>
<tr>
<td>$\alpha$</td>
<td>0.11</td>
<td>0.14(3) $^\ast$</td>
<td>0.17(9)$^\ast$</td>
<td>0.14(6)$^\ast$</td>
<td>0.28(12)$^\ast$</td>
<td>0.47(12)$^\ast$</td>
<td>0.18(2)</td>
</tr>
<tr>
<td>$\beta$</td>
<td>0.34</td>
<td>0.31(2)</td>
<td>0.30(3)</td>
<td>0.31(3)</td>
<td>0.23(3)</td>
<td>0.19(2)</td>
<td>0.238(5)</td>
</tr>
<tr>
<td>$\gamma$</td>
<td>1.24</td>
<td>1.25(2)</td>
<td>1.20(6)</td>
<td>1.23(3)</td>
<td>1.26(6)</td>
<td>1.40(6)</td>
<td>1.36(3)</td>
</tr>
</tbody>
</table>

Table 6.2: See Table 6.1 for details. Critical parameters of the ANNNI model for $\kappa > \kappa_L$ obtained by finite-size scaling of systems with $L_z = 60, 120, 150, 180,$ and 240 at $\kappa = 0.522, L_z = 120, 240,$ and 360 at $\kappa = 0.7, L_z = 60, 100, 120, 200,$ and 240 at $\kappa = 0.8, L_z = 60, 120, 180,$ and 240 at $\kappa = 2.0,$ and from previous simulations [4, 5]. XY values are given for reference.

<table>
<thead>
<tr>
<th>$\kappa$</th>
<th>XY [146]</th>
<th>0.5 [4]</th>
<th>0.522</th>
<th>0.6 [5]</th>
<th>0.7</th>
<th>0.8</th>
<th>2.0</th>
</tr>
</thead>
<tbody>
<tr>
<td>phase</td>
<td>–</td>
<td>$\langle 3 \rangle$</td>
<td>$\langle 3 \rangle$</td>
<td>$\langle 2^{13}3^{4} \rangle$</td>
<td>$\langle 2^{13}3^{4} \rangle$</td>
<td>$\langle 23 \rangle$</td>
<td>$\langle 2^{13} \rangle$</td>
</tr>
<tr>
<td>$q_c^{MC}$</td>
<td>–</td>
<td>0.17(3)</td>
<td>0.167(4)</td>
<td>0.18(3)</td>
<td>0.192(4)</td>
<td>0.200(4)</td>
<td>0.233(4)</td>
</tr>
<tr>
<td>$q_c^{HT}$</td>
<td>–</td>
<td>0.162(1)</td>
<td>0.167(1)</td>
<td>0.180(1)</td>
<td>0.192(1)</td>
<td>0.200(1)</td>
<td>0.232(1)</td>
</tr>
<tr>
<td>$q_c^{MF}$</td>
<td>–</td>
<td>0.1667</td>
<td>0.1705</td>
<td>0.1816</td>
<td>0.1919</td>
<td>0.1994</td>
<td>0.2301</td>
</tr>
<tr>
<td>$T_c^{MC}$</td>
<td>2.202</td>
<td>3.6(1)</td>
<td>3.723(1)</td>
<td>3.82(3)</td>
<td>3.988(1)</td>
<td>4.141(1)</td>
<td>5.796(1)</td>
</tr>
<tr>
<td>$T_c^{HT}$</td>
<td>2.202 [214]</td>
<td>3.67(2)</td>
<td>3.72(2)</td>
<td>3.81(2)</td>
<td>3.99(3)</td>
<td>4.14(1)</td>
<td>5.79(1)</td>
</tr>
<tr>
<td>$\nu$</td>
<td>0.67</td>
<td>–</td>
<td>0.66(2)</td>
<td>–</td>
<td>0.67(4)</td>
<td>0.66(2)</td>
<td>0.67(3)</td>
</tr>
<tr>
<td>$\alpha$</td>
<td>-0.01</td>
<td>–</td>
<td>0.02(6)$^\ast$</td>
<td>–</td>
<td>-0.01(9)$^\ast$</td>
<td>0.02(6)$^\ast$</td>
<td>-0.01(9)$^\ast$</td>
</tr>
<tr>
<td>$\beta$</td>
<td>0.35</td>
<td>–</td>
<td>0.35(2)</td>
<td>–</td>
<td>0.35(3)</td>
<td>0.34(3)</td>
<td>0.36(2)</td>
</tr>
<tr>
<td>$\gamma$</td>
<td>1.32</td>
<td>–</td>
<td>1.30(4)</td>
<td>–</td>
<td>1.32(8)</td>
<td>1.33(4)</td>
<td>1.32(6)</td>
</tr>
</tbody>
</table>

A change of the average local magnetization at position $i$ is equivalent to shifting the phase angle $q_{zi}$ with respect to that profile. Note that the isotropic nature of the critical PM transition suggests that pairs of spins parallel and perpendicular to the $z$ axis are equivalently correlated, i.e., the $z$-axis magnetization profile itself is correlated in the $x$ and $y$ directions. In the language of XY model, the phase angle is also correlated under...
translations in the $x$ or $y$ directions.

Why then, one may wonder, do the series expansion results not converge to the right $\gamma$ value at high $\kappa$? Examining the limit $\kappa \to \infty$ suggests an answer. In that limit the next-nearest neighbor interaction dominates and the spins decouple into series of intercalated 1D Ising antiferromagnetic chains. That singular limit has 1D Ising universality for which $\gamma = 1$. The finiteness of the HT series expansion thus results in a slow decay of $\gamma$ toward unity, as the large $\kappa$ terms in the series dominate the expansion. In this respect, the series is both a high temperature and low $\kappa$ expansion, which further restricts its range of validity.

6.6 ANNNI Roughening Transition

In the Ising ferromagnetic regime, even though the correlation length isotropically diverges at the critical point, the interface between two regions of opposite magnetization presents a roughening transition $T_R$ at roughly half the critical temperature [14, 217–219]. Below $T_R$ the interface is localized, while above $T_R$ its width diverges logarithmically with surface area. In simulations, an interface is created within the bulk by using an antiperiodic boundary condition along the $z$ direction [217] and the transition can be localized by finite-size analysis (Fig. 6.4). Modulated phases present a series of interfaces between lamellae of opposite magnetization that may also roughen with increasing temperature. It has indeed been suggested that the interface location of modulated lamellae should logarithmically diverge [44, 220]. If that were the case, interlayer fluctuations at temperatures between $T_R$ and $T_c$ could participate in phase branching and the formation of equilibrium incommensurate structures in the large system limit [221].

A generalization of the simulation approach is necessary to study this question.
The variance of the interface position \( z \)

\[
W^2 \equiv \langle (z - \langle z \rangle)^2 \rangle \tag{6.3}
\]

measures the fluctuations of the interface location, and is expected to diverge logarithmically with system size for \( T > T_R \)

\[
W^2 \sim \ln L_\perp. \tag{6.4}
\]

For \( T < T_R \), \( W^2 \) should have an even weaker system size dependence. In practice, the average in Eq. 6.3 is taken over the normalized magnetization gradient

\[
g(z) = \frac{(ds_{xy}(z)/dz)}{\int(ds_{xy}(z)/dz)dz} \tag{6.5}
\]

\[
= \frac{s_{xy}(z + 1) - s_{xy}(z)}{\sum_{z}[s_{xy}(z + 1) - s_{xy}(z)]}, \tag{6.6}
\]

used as weight function [222]. The equilibrium profile \( s_{xy}(z) \) is obtained by aligning instantaneous profiles to correct for lattice drift before averaging (Fig. 6.4). For the modulated regime, where multiple interfaces are present, layers within half a period of the interface \( i \), i.e., layers whose \( z \) coordinates belong to a set \( I \), are grouped together in the variance calculation

\[
W_i^2 = \sum_{z \in I} z^2 g(z) - \left( \sum_{z \in I} z g(z) \right)^2, \tag{6.7}
\]

and the results for the various interfaces are averaged at the end.

We first consider the impact of frustration on the roughening transition of the ANNNI model in the ferromagnetic regime (Fig. 6.4). Although the \( T_R \) values extracted from simulations are quantitatively different from the series expansion results [14], similar trends are observed (Figs. 6.5). In particular, the transition temperature \( T_R \) is relatively invariant to increases in frustration. The formation of an interface is not further stabilized by frustration, but rather decreases with increasing \( \kappa \).
And contrary to the scenario predicted for other microphase-forming systems [223], the roughening transition does not pass through or near the Lifshitz point. Instead, the roughening transition line on the $T$-$\kappa$ phase diagram is expected to reach the FM phase boundary near $\kappa \simeq 0.43$. Interestingly, a finite-temperature intercept suggests that the FM transition may be markedly different above and below $T_R$.

It has also been suggested that a roughening transition might be observed for the modulated phases as well [220, 223]. For the ANNNI model, however, we find no indication of interfacial roughening, at least for two simple modulated phases: phase $\langle 2 \rangle$ at $\kappa = 0.8$ and phase $\langle 3 \rangle$ at $\kappa = 0.52$ (Fig. 6.4). For the latter, the interface location remains clearly defined at all $T < T_c$, even for the largest systems considered. It cannot be excluded that a divergence may be observed for much larger interfacial areas than those we studied. Yet the lattice is here at least an order of magnitude larger than the size necessary for detecting roughening in the ferromagnetic phase (Fig. 6.4). We venture to speculate that, at least on a lattice, the persistence length of the lamellae might be very large, and possibly infinite. If that were the case, the roughening of the modulated layers would then coincide with $T_c$. Further simulation and theoretical work are, however, necessary to clarify the situation.

6.7 ANNNI Phase Diagrams

Detailed low $T$ series expansion studies of the phase behavior around $\kappa = 1/2$ conducted by Fisher et al. [98, 212] suggest that a series of “simple phases” of the form $\langle 2^{j/3} \rangle$ spring out from the the multiphase point at $T = 0$ and “mixed phases” generated by combinations of neighboring simple phases branch out at $T > 0$. The temperatures accessible in simulations are relatively far from the regime of validity of this theory and thus, from this point of view, it is misleading to compare them directly. It is nonetheless interesting to note that the two approaches appear to converge for $T \lesssim 2$. 

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Figure 6.4: Left: The roughening transition in the ferromagnetic regime at $\kappa = 0.2$ using systems of size $L^2 \times 26$ is found at $T_R = 2.35(5)$. (insets) Average magnetization profile and gradient at $T = 3.5$. Right: Interface width $W^2$ of phase $\langle 3 \rangle$ of the ANNNI model at $\kappa = 0.52$ as a function of $T$ for various system sizes $L^2 \times 36$. No roughening transition is detected within the stability regime. The magnetization profile $s_{xy}(z)$ for the system of $L = 128$ at $T = 3.0$ is also shown (left inset) along with its normalized gradient $g(z)$ (right inset).

Various approximate theoretical treatments have been used to analyze the ANNNI phase diagram more globally. In addition to the traditional mean-field approach [99], an effective field [100] and a tensor product variational approach (TPVA) [12] have more recently been used. These last two approaches reasonably capture the external boundaries of the modulated regime. The two treatments, however, qualitatively disagree on the internal structure of that same regime. On the one hand, the effective-field method [100], like the mean-field treatment and the soliton approximation [99], fills the modulated interior by exceptionally stable bulging simple phases, such as phase $\langle 3 \rangle$ phase and phase $\langle 23 \rangle$ (Fig. 6.5). On the other hand, TPVA predicts rather narrow stability wedges for the commensurate phases [12]. The simulation results tend to favor the second scenario. Although the devil’s staircase indicates that the rate of wave number change slows on approaching $T_c$, only the antiphase has a broad presence in the modulated regime. The stability range of the different modulations is fairly small, and all of the phases commensurate with the periodic box are stable in turn. The branching and mixing of the stable low-temperature $\langle 2^j 3 \rangle$ phases
Figure 6.5: $T$-$\kappa$ phase diagram of the ANNNI model. Phase boundaries are obtained from $U_4^*$ (□) and $F$ (⊙). The Lifshitz point location (●) is taken from Ref. [2]. High- [3, 10] and low-temperature [11] series expansions as well as TPVA [12] results are represented. The stability wedges of phases $\langle 3 \rangle$ and $\langle 23 \rangle$ obtained from simulation are seen to be qualitatively different from the mean-field theory predictions (right inset) [13]. The roughening transition results in the ferromagnetic regime are similar to the series expansion results [14].

is already complete at the temperatures studied here [59, 212]. In particular, no special stability is observed for phases $\langle 3 \rangle$ and $\langle 23 \rangle$ (Fig. 6.5). For phase $\langle 3 \rangle$ some bulging is seen, because of the slower rate of change of the periodicity near $\kappa = 1/2$.

Simulating larger lattices, which allow for a more refined $q$ selection, however shrinks that phase’s footprint. For phase $\langle 23 \rangle$, the range of stability does increase slightly with $\kappa$, but the effect seems to be due to the finiteness of the lattice. In any case, the increase is much less pronounced than the bulging scenarios predict [99, 100]...
For the IC model, qualitatively similar branching is expected in the devil’s flower region, which is found between phases of integer periodicity. The systems simulated here are, however, too small to examine this issue critically. Except for the caveats presented in the previous sections, our results mostly agree with the simulation results of Ref. [6].

6.8 ANNNI Model under Shear

Using the algorithm described in Sec. 5.10, we study the effect of shear on the lamellar phases formed by the ANNNI model. We choose the $q = 0.18$ modulated phase in a $200 \times 40^2$ system at $\kappa = 0.6$. It is necessary to sample the system after it reaches the steady state. As shown by the energy evolution in Fig. 6.6a, higher shearing rates lead to longer waiting time. After the steady state is reached, we calculate the energy, structure factor and heat capacity at various shearing rates. The results suggest that shearing can postpone the melting of the ordered lamellae as temperature increases (Fig. 6.6d). At the same temperature, the structure factor of the modulated phase is higher at higher shearing rate, which indicates the periodic pattern is enhanced by shearing compared to a static lamella (Fig. 6.6c). These observations agree with the theoretical predictions [67].

As discussed in Ref. [67], shear can reduce the influence of nonlinear fluctuations, which are the cause of a lowered transition temperature in the static case. A study on 2D Ising model suggests that the effect may result from three mechanisms, shear-enhanced cluster growth, cluster coalescence and cluster breakup.

6.9 Conclusion

In this chapter, we have clarified the structure and transition properties of the modulated regime of the ANNNI and the IC models. Previous theoretical treatments had
sometimes been insufficient, particularly concerning the stability regime of the various modulated phases, the critical nature of the ANNNI PM transition, and the role of roughening. The isotropic nature of the critical behavior of the ANNNI model beyond the Lifshitz point, despite the existence of anisotropic interactions and phases, is an interesting result that deserves future considerations. In the case of lamellar phase roughening, no clear conclusion can be drawn, but our results suggest that the phenomenon is at least a lot less pronounced than in the Ising model, which may give hope of experimentally forming microphase patterns on much larger scales than previously thought. From a theoretical perspective, it is also interesting to highlight,
however, that mean-field theory is particularly adept at predicting the periodicity of modulated phases at the PM transition. This observation may explain why the approach has been so successful at describing order in other microphase-forming systems, such as diblock copolymers [26, 224].

In addition to lamellar phases, modulated assemblies can exhibit a variety of other symmetries. They can also be observed off lattice. Generalizing the approach to continuous space and to other order types would thus greatly benefit the study of more complex microphase-forming systems. For the IC model, it could for instance help determine the nature of the modulated-Néel transition and other properties of the high $Q$ regime, which we have only briefly explored. Completing the simulation tool set would also pave the way for studies of the non-equilibrium microphase assembly, where most of the materials challenges lie.
Results of the SWL Model

In this chapter we present the preliminary work we have done on the simulation of microphases in the SWL model.

7.1 Simulation Details

We test the thermodynamic integration method (Sec. 5.6.2) for the SWL model with \( \lambda = 1.5, \kappa = 4 \) and \( \xi = 0.2 \) at \( T = 0.2 \) and \( \rho = 0.5 \). Systems of \( N = 1000\text{-}2000 \) particles are prepared in boxes whose relative dimensions are allowed to vary. The cutoff \( r_{\text{cut}} \) is set to \( \kappa \) for the SWL and \( \sigma \) for hard spheres under field (HSF). In order to check the validity of the method, fields with strength \( B_0 = 2 \) and 3 are used. For volume fluctuations in the \( NpT \) simulation of HSF, one of the three box dimensions is randomly chosen to change once every MC step. To prepare a modulated phase, we start from a uniform hard sphere liquid under a field with the right periodicity and use the equilibrium configuration to initialize the SWL system.
Figure 7.1: Left: equation of state of HSF with \( n = 4 \) using different field strength \( B_0 \). The vertical dotted line marks the end point of the integration \( \rho = 0.5 \). Right: free energies as a function of \( q = n/L_z \) for \( L_z = 19, 20, 21, 22 \) and \( n = 3, 4, 5 \).

7.2 Lamellar Phases

We first calculate free energies for lamellar phases with \( L_z = 19, 20, 21, 22 \) and \( n = 3, 4, 5 \), where \( n \) is the number of periods in the simulation box. For the integration from free particles under field to HSF at \( \rho = 0.5 \), we use \( NpT \) simulations to obtain the equation of state as in Fig. 7.1. As expected, for a same density, a stronger field \( B_0 \) results in a higher pressure, because particles inside each of the domains are more densely packed. The total free energy of a lamellar phase with \( L_z = 20 \) and \( n = 4 \) obtained from different field strength is found to be in good agreement with each other, as compared in Table 7.1. The free energy as a function of wave number \( q = n/L_z \) shows that the most stable lamellar phase is \( q = 4/21 \approx 0.1905 \) (Fig. 7.1 and Fig. 7.2).

7.3 Cylindrical Phases

Although we have identified the most stable lamellar phase at \( T = 0.2 \) and \( \rho = 0.5 \) above, the real equilibrium phase can be of other morphologies. We thus calculate the free energy of possible cylindrical phases. We prepare a cylindrical phase by placing
Table 7.1: Free energy results of a SWL lamellar phase with $L_z = 20$ and $n = 4$ using a field $B = B_0 \cos(kz)$, $k = 2\pi n/L_z$.

<table>
<thead>
<tr>
<th>$B_0$</th>
<th>$f^\infty_0 = -k_BT \ln I_0(\beta B_0)$</th>
<th>$df_1^a$</th>
<th>$df_2^b$</th>
<th>$f = f^\infty_0 + df_1 + df_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>-2.547133822</td>
<td>1.618</td>
<td>-1.385911</td>
<td>-2.315</td>
</tr>
<tr>
<td>2</td>
<td>-1.588594417</td>
<td>1.252</td>
<td>-1.965485</td>
<td>-2.302</td>
</tr>
</tbody>
</table>

$a$ from free particles under field ($\rho = 0$) to HSF at $\rho$

$b$ from HSF at $\rho$ to SWL at $\rho$

Figure 7.2: Left: lamellar phase with $L_z = 21$ and $n = 4$. Right: cylindrical phase with $a = 7.216878$.

2000 particles in a simulation box of size $L_x = 25$ and $L_y = 25 \times \frac{3}{2\sqrt{3}} = 21.650635$. In the notation of Sec. 5.6.2, this choice means setting $n = 2$ and assigning $m = 3$ domains in the $y$ direction. The lattice constant between domains is then $a = L_x/\sqrt{3}n = 7.216878$ (Fig. 7.2).

Simulations of this cylindrical phase show that its energy and free energy are far below those of the lamellar phase considered above. However, equilibrating this phase is extremely difficult at $T = 0.2$. By scanning over temperatures, we find that the cylinders finally melt at $T > 0.5$. To accurately calculate the free energy of the cylindrical phase at low temperatures, simulations longer than $10^6$ MC cycles are thus required at such low temperatures.
7.4 Conclusion

We have tested the validity of the TI algorithm in the SWL system. Lamellar phases at $T = 0.2$ and $\rho = 0.5$ are studied and optimized. A preliminary calculation of the cylindrical phase shows that it is more stable than lamellar phases at that phase point. This illustrates that an apparently stable modulated phase in a particle system may not be the global equilibrium one, unless the free energy is optimized. To complete the study of the SWL phase diagram, more efficient simulation algorithms will be needed.
Results of the GEM-4

In this chapter, we report the low temperature equilibrium phase properties of the GEM-4. In particular, we find first-order isostructural transitions between cluster crystals of integer occupancy. Using $[N]pT$ ensemble simulations, we study the critical properties of this transition.

8.1 Simulation Details

We perform Monte Carlo simulations using the approach of Ref. [225] of the GEM-4 model, whose high-temperature behavior was previously determined [15], for $N = 1000$-$5000$ particles at constant $N$, volume $V$, and temperature $T$. The pressure $p$ is obtained from the virial and the (constrained) Helmholtz free energy $F$ of the different phases is calculated via thermodynamic integration. For a fixed number density $\rho$, the average lattice site occupancy $n_c$ at equilibrium is identified for every state point by simulating crystals at various fixed $n_c$ then minimizing the resulting constrained free energy $f_c(n_c) \equiv F_c(n_c)/N$ (Fig. 8.1), similarly to the scheme used for GEM-4’s high-$T$ phase diagram determination [15]. In the latter, $n_c$ was tuned until the (unphysical) field conjugate to $n_c$ had vanished [15, 85], which allows for a
gradient-based minimization of $f_c$, but relies on an additional independent calculation of the chemical potential $\mu$. This approach breaks down at low $T$, where $\mu$ cannot be efficiently resolved by Widom’s particle insertion [16], which places the ghost particle at random positions. But at low temperatures only insertions occurring around the lower-occupancy sites can be successfully accepted. Phase coexistence is then determined through common tangent construction of the equilibrium free energy data, or of its linear transform $\tilde{f}_\rho = \beta f_\rho - \kappa \rho$ in practice (Sec. 4.3) (Fig. 8.2).

8.2 GEM-4 Phase Diagram

We present two projections of the low-$T$ phase diagram in Fig. 8.1. As anticipated from the high-$T$ extrapolation, the cluster BCC phase vanishes at a triple point $T^{(1)}_t = 0.078(1)$. But surprisingly the transition is preceded by a S-shaped doubly
Figure 8.2: Free energy curves of the stable FCC (⊙) and, for comparison, the metastable BCC (▽) structures at $T = 0.01$ with $\kappa = 142.7$ (Sec. 4.3). Both curves show the van der Waals loop characteristic of a system whose limited size inhibits phase separation. The coexistence densities of the FCC1 (left inset)-FCC2 (right inset) isostructural transition are determined by the common tangent construction (dashed line). The equilibrium lattice occupancy $n_e^{eq}$ (●) plateaus near integer values for the thermodynamically stable phases.

Reentrant (SDR) crystal phase sequence, where both a maximum and a minimum in the coexistence curve are observed. Below $T_t^{(1)}$ the phase diagram is surprisingly rich. GCM-like phase behavior [78–80] is followed by an unexpectedly complex clustering regime (Sec. 1.2 and Sec. 2.5). Because the tail of the GEM-4 decays faster than any inverse power, the liquid freezes into a single-occupancy FCC (FCC1) that reaches vanishingly small densities at low $T$, in agreement with predictions from genetic algorithms [179, 226] and phonon theory [17]. This FCC1 phase gives way to a single-occupancy BCC (BCC1) phase at a second triple point $T_t^{(2)} = 0.031(1)$. For a narrow temperature range above $T_t^{(2)}$, a BCC1 wedge between the liquid and the FCC1 phase leads to reentrant crystallization of BCC1 upon compression. The liquid-BCC transition has also been observed for soft inverse power potential $u(r) \sim 1/r^n$ with $n \leq 7$ [227]. Because BCC is more loosely packed and thus has more vibrational entropy compared to close-packed structures, it appears first below the melting line.
at higher temperatures [228]. Even if FCC is stable, BCC can still be the first structure to nucleate [229]. But for steeper repulsion, BCC is mechanically unstable to shear [230]. The maximum freezing temperature for BCC1 at $T = 0.039(1)$ leads to a second SDR sequence similar to that observed in the hard core/soft shoulder model [150, 231]. By contrast to the GCM’s reentrant melting behavior [78–80], here the liquid reentrance section of the SDR sequence spreads only over a finite density regime $0.59 \lesssim \rho \lesssim 0.68$ and over a much smaller temperature range $0.0385 \lesssim T \lesssim 0.039$. The intermediate nature of the GEM-4 suggests that this reentrance might become more pronounced as the GCM is approached, i.e., $n \to 2^+$, and should disappear before the PSM limit $n \to \infty$, where reentrance is not expected [20]. The connection between the high and low-$T$ regimes occurs through a third triple point $T^{(3)}_t = 0.040(1)$, at which BCC1 vanishes. A prior, coarser study of the liquid-crystal transition in this regime missed both the presence of FCC1 and of the reentrant melting [232]. It also inaccurately assigned the unusual shape of the liquid-crystal coexistence curve to the onset of clustering, while it is caused by the reentrant melting.

Clustering does indeed influence the phase diagram topology, but at densities further away from the liquid phase. At low $T$ the nature of clustering is unlike what is seen at higher $T$, where $n_c$ changes linearly with $\rho$ resulting in a nearly density independent lattice constant [15]. Here, $n_c$ is quasi-quantized, and at very low $T$ the lattice constant $a$ changes discontinuously through isostructural transitions between FCC lattices of nearly perfect integer mean occupancy $n_c \leftrightarrow n_c + 1$ (Figs. 8.2-8.3). The first occurrence of these transitions, FCC1 $\leftrightarrow$ FCC2, is partially interrupted by the BCC1 phase, down to the fourth triple point $T^{(4)}_t = 0.012(1)$ (Fig. 8.1). But at higher densities, the FCC2 $\leftrightarrow$ FCC3 coexistence is fully developed. No other liquid or crystal phases are found to interfere and genetic algorithm results corroborate that no other crystal symmetry should be stable in this density regime [179, 226].
Figure 8.3: Isothermal \((T = 0.03)\) bulk modulus \(B\) (○), its virial contribution (●) and softening correction (shaded), and \(n^\text{eq}\) (▽). The solid vertical lines indicate phase boundaries. The lattice constant \(a\) changes discontinuously as FCC2→FCC3 (inset).

It is at the moment computationally difficult to go beyond FCC3, but both a zero temperature treatment paired with phonon theory [17] and a simple mean-field cell theory predict a cascade of \(n_c \leftrightarrow n_c + 1\) isostructural transitions to carry on \(ad\ in\-finitum\), slightly broadening the coexistence regime between two integer occupancies. As argued above, the topology of the phase diagram demands that each uninterrupted isotructural transition terminates at a critical point, the first one of which is found at \(T_c^{(2,3)} = 0.049(3)\) (see Sec. 8.4 for more details). Hopping between lattice sites should depress \(T_c^{(n_c,n_c+1)}\) as \(n_c\) increases. The series of first-order isostructural transitions contrasts with the continuous second-order clustering transitions for the PSM predicted by cell theory [20] (Sec. 9.2). This last observation suggests that the behavior of the PSM might be singular, but further studies are necessary to clarify the GEM-\(n\) family phase behavior as \(n \to \infty\).
8.3 Bulk Modulus

One of the key material properties of cluster crystals is the presence of two distinct microscopic mechanisms for responding to compression. Like any other crystal, cluster crystals can affinely reduce their lattice constant, but additionally they can eliminate lattice sites by increasing the mean lattice occupancy. We can decompose the bulk modulus $B \equiv V \left( \frac{\partial^2 F}{\partial V^2} \right)_{N,T} = B_{\text{vir}} - B_{\text{corr}}$ into a constant $n_c$ virial contribution $B_{\text{vir}}$ and a “softening” correction $B_{\text{corr}}$, which map directly to the two microscopic mechanisms [15, 126] (Sec. 3.1.1). At high $T$, $B_{\text{corr}}$ can be as high as half the virial component [15], but in low $T$ crystals, the quasi-quantized jumps in $n_c$ lead to a significantly different mechanical behavior. Away from the coexistence regions, where $n_c$ is nearly constant, the system responds only affinely to isothermal compression and the virial contribution to the bulk modulus captures the full response of the system, i.e., $B_{\text{corr}} \sim 0$, (Fig. 8.3)$^1$. But in the softening regions that precede and follow the phase transitions the quantization is imperfect, and $B_{\text{corr}} \neq 0$. Near the BCC1-FCC2 transition, for instance, $B_{\text{corr}}$ is nearly equal to the virial contribution, which means that the system exerts almost no resistance to compression. This very rapid change in mechanical properties with compression is uncommon, and may lead to novel material behavior. The different physical natures of the virial and softening contributions indeed suggest a separation of time scales for their microscopic relaxation, with slow particle redistributions contrasted by fast affine deformations. Hardening or softening of the material upon compression might thus depend on the deformation rate.

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$^1$ The bulk modulus is obtained by differentiating empirical fits to the free energy results. Though this approach captures the mechanical behavior rather well, some numerical errors remain since the softening correction must clearly be positive.
Figure 8.4: $[N]pT$ simulations of the GEM-4 with $N_c = 1372$ at $T_0 = 0.045$ and $p = 1.97$. Left: particle number oscillates within the bounds $[3000, 3800]$. The thick vertical lines mark the iterations. Right: optimization of the field $\tilde{g}_N$, which should converge to the double-well Gibbs free energy.

8.4 $[N]pT$ Simulations of the Isostructural Critical Point

Although particle insertion is difficult at very low temperatures, as we will study in more details in Chapter 9, it is nonetheless reasonable to apply the $[N]pT$ ensemble method at temperatures close to $T_c$ of the isostructural transition, because the lattice constant of the two phases there is very similar. We perform $[N]pT$ simulations of various system sizes $N_c = 500, 864, 1372$ at $T_0 = 0.045$ and $p = 1.97$ to study the isostructural critical point between phases FCC2 and FCC3. The double-well Gibbs free energy curve obtained from thermodynamic integration is used as the initial guess for the field $\tilde{g}_N$. The particle number oscillates almost uniformly within the window in the first few iterations (Fig. 8.4). We expect $10^7$ MC cycles to provide good statistics. After the distribution of $N$ has completely flattened, $\tilde{g}_N$ should converge to the constraint Gibbs free energy per particle $g_c$ with two wells corresponding to the two coexistence densities (Fig. 8.4). At coexistence temperature and pressure, the minima of the two wells are of equal height, giving an equal chemical potential for the two phases.

We then use histogram reweighting to obtain $g_c$ at higher temperatures. Be-
cause the coexistence pressure changes with temperature, one needs to do histogram reweighting over pressures until the two wells become of same height all along. With this scheme, we determined a series of coexistence densities of the FCC2-FCC3 isostructural transition close to the critical point (Fig. 8.6).

We can extract the critical temperature in the infinite system using finite-size scaling [205]. For different system sizes $L \propto N_c^{1/3}$, the distributions $\mathcal{P}_L(\rho = N/\langle V \rangle) \sim e^{\beta(\mu^{eq}N-G_c)}$ at their apparent critical temperature $T_c(L)$ as a function of $x = L^{\beta/\nu}(\rho - \rho_c(L))$ collapse onto a universal function, if the right critical parameters $T_c(L)$, $\rho_c(L)$ and $\beta/\nu$ are chosen [205]. We use the Ising universality [18] and obtain good scaling behaviors (Fig. 8.5). Using the scaling laws (Eq. 5.92), we then estimate the critical values $T_c(\infty) = 0.0470(2)$ and $\rho_c(\infty) = 1.2400(3)$ for the FCC2-FCC3 transition (Fig. 8.6).

8.5 Conclusion

We have presented the intriguing low-temperature phase behavior of the cluster-crystal-forming GEM-4. The complexity of the phase behavior is particularly note-
Figure 8.6: First-order FCC2-FCC3 isostructural transition of the GEM-4. Previous thermodynamic integration (TI) results [19] are shown for comparison. $[N]pT$ simulations with histogram reweighting and finite-size scaling estimate $T_c(\infty) = 0.0470(2)$ and $\rho_c(\infty) = 1.2400(3)$.

Worthy considering the simplicity of the model, which is free of competing length scales. Experimental soft matter realizations of cluster crystals are still lacking, but large-scale, monomer-resolved simulations of amphiphilic cluster-forming dendrimers have further demonstrated possibilities of making such materials [74]. Importantly, the approach outlined in the present work should be directly applicable to phenomena of reversible cluster formation in other branches of physics. Examples are: the structures formed by the soft solitons [233, 234], the quasi-2D electron bubbles in the quantum-Hall regime [235, 236], and the predicted clustering of vortex lines in rotating Bose gases [237].
In this chapter, we apply the $[N]pT$ ensemble simulation to the PSM and obtain its equilibrium phase properties. At low temperatures, the liquid-solid transition goes to the HS limit with a crossover around $T \sim 0.1$. At higher densities, occupancies are found to change continuously, rather than following a series of isostructural transitions as in the GEM-4.

9.1 Simulation Details

For the $[N]pT$ high temperature simulations, $4 \times 10^4$ Monte Carlo (MC) cycles are performed for $N = 1000–5000$ particles at each iteration. Each cycle contains on average $30\% N$ particle number changes, $70\% N$ particle displacements and one volume fluctuation. For the crystal phase, the particles are spread over $N_c = 256–1372$ lattice sites depending on the average occupancy. A particle range of $\Delta N \equiv N_{\text{max}} - N_{\text{min}} = 150–200$ is found to provide a reasonable trade off between the need to correctly estimate the equilibrium occupancy and the computational cost. The histogram of states separates volume fluctuations in 50 bins and energy fluctuations in 500 bins that span the observed range of fluctuations. For most system sizes studied, the range has
$V_{\text{max}} - V_{\text{min}} \sim 50$ and $E_{\text{max}} - E_{\text{min}} \sim 2000$. The summation over these states is done on logarithmic scale to avoid numerical overflow [196].

A good initial guess for the weights is the chemical potential of a system with $N_0 \in [N_{\text{min}}, N_{\text{max}}]$, $\tilde{g}_N = \mu(N_0)$, obtained by Widom insertion in a short $NpT$ simulation [16]. From this point on, fewer than ten iterations are needed to converge the standard deviation of the equilibrium probability distribution within $\sigma_{P_N} \simeq 0.001$. Even though the resulting weights are noisy for a given $N$, considering the full $N$ range by, for instance, fitting them with a parabola smooths out these uncorrelated fluctuations. After including the offset $C$, the constrained Gibbs free energy thus has an approximate form

$$G_c = c_2 N^2 + c_1 N + c_0,$$

where $c_0$, $c_1$, and $c_2$ are numerically determined. Correspondingly,

$$g_c = c_2 N + c_1 + c_0/N,$$

$$\mu = 2c_2 N + c_1,$$

and

$$\mu_c = -\frac{c_2}{N_c} N^2 + \frac{c_0}{N_c}.$$

If appropriate bounds are chosen, $g_c$ is then minimized at $N^{\text{eq}} = \sqrt{c_0/c_2} \in [N_{\text{min}}, N_{\text{max}}]$. Figure 9.1 illustrates this operation. Starting with $\mu(N_0 = 3910) = 15.784672$, the simulation converges to $\tilde{g}_N$. After including the constant offset $C = 397$, $g_c$ is minimal at $N^{\text{eq}} = 3965(10)$ ($n_c = 7.93(1)$), where the error is obtained from running several optimizations of $\tilde{g}_N$. The equilibrium particle number obtained by this method is in good agreement with that determined by pure thermodynamic integration, $N^{\text{eq}} = 3960(10)$, following the approach described in Ref. [19]. This particular example also illustrates that the minimum of $g_c$ need not correspond to that of $\tilde{g}_N$, and can even be out of the chosen range $[N_{\text{min}}, N_{\text{max}}]$, although for the minimization to be reliable within the accuracy reported here the range should be chosen such that the minimum does fall within those bounds.
Determining the equilibrium behavior from the free energy requires a fairly high degree of numerical accuracy. It is thus worth estimating the error made in this process. The typical change in weight values over the full $N$ interval $\Delta g_c$, is smaller than the shift from $\tilde{g}_N$ to $g_c$. For instance, over an interval of length $\Delta N \sim 10^2$, $\Delta g_c \sim 10^{-3}$. The Gibbs free energy per particle, which is of order $10^2$, is determined by thermodynamic integration with an error $\delta g_0 \sim 10^{-2}$. The offset constant $C$ will thus have an error $\delta C = \delta g_0 N_0 \sim 10^{-2} \times 10^3 = 10^1 \sim \delta c_0$. The error $\delta g_c$ in $g_c$ is then of order $10^{-2}$, which is an order of magnitude larger than the variation $\Delta g_c$. Yet the position of the minimum of the curve, $N^{eq} = \sqrt{c_0/c_2}$ is only shifted by $\delta N^{eq} \sim N^{eq}(\sqrt{1 + \delta c_0/c_0} - 1) \sim 10^3 \times 10^{-3} = 10^0$. Therefore, although the error in the vertical shift of $g_c$ may be an order of magnitude larger than the shallowness of the curve itself, the position of the minimum is preserved with an accuracy comparable to that obtained from running multiple instances of the optimization.
9.1.1 Low-Temperature Implementation

Special attention needs to be drawn to use the \([N]pT\) method for the PSM at relatively low temperatures, \(T < 0.1\). First, the traditional volume fluctuation algorithm fails to sample low-temperature compressions of the PSM. To overcome this problem, we use the Schultz-Kofke algorithm [178], as discussed in Sec. 5.4.

Second, particle insertion also becomes difficult at low temperatures. For low \(T\) crystals with an occupancy intermediate between two integers, new particles can only be successfully inserted at the lower-occupancy positions. Modified particle insertion schemes, such as the staged-insertion algorithm designed for fluid phase [183, 238], do not help, because the problem is intrinsic to the system. Inserting particles requires one to randomly identify a vacancy in the crystal, which constrains the \([N]pT\) approach at low \(T\) to crystals with non-integer occupancy. Once these regions are identified, PSM crystals with integer occupancy can then be treated using standard \(NpT\) simulations. For the \([N]pT\) scheme at low \(T\), the chemical potential used as initial guess for \(\tilde{G}_N\) is obtained from staged Widom insertion [182, 183] (Sec. 5.5), and \(10^6\) MC cycles are needed at each iteration to obtain good statistics. To speed up the simulations, more particle insertions and deletions (50\%\(N\)) and ten to a hundred times fewer volume fluctuations are used in each cycle. The particle number window is also shortened to \(\Delta N = 50\). Yet the inherently low efficiency of particle insertion in low \(T\) cluster crystals leaves the \([N]pT\) approach less efficient than the free energy integration scheme of Ref. [19]. Only a few state points were thus equilibrated this way. The rest were obtained using multiple thermodynamic integrations to locate the free energy minimum [19].
9.2 Equilibrium Cluster Crystal Properties

We first identify the equilibrium cluster crystal occupancy \( n_{eq} \) at different phase points. Qualitatively, \( n_{eq} \) increases with density and pressure, and at fixed pressure the number of particles per cluster decreases with increasing temperature as new lattice sites are formed. Quantitatively, at fixed high \( T \), \( n_{eq} \) grows roughly linearly with density, while at fixed density, it grows linearly with temperature (Fig. 9.2(a)).

If viewed as a function of \( \rho \) and \( T \), \( n_{eq}(\rho, T) \) has a bilinear form \( n_{eq} = aT + b\rho + c \) with positive \( a \) and \( b \), and a small \( c \). The DFT prediction, \( n_{eq} = 2T + \rho \) [22], is qualitatively comparable with the coefficients obtained from fitting the simulation results (Fig. 9.2(a)), but in order to capture the clustering behavior for temperatures as low as \( T \sim 0.1 \), quadratic corrections are necessary.

As \( T \) is further lowered, \( n_{eq} \) plateaus at integer occupancy values, which we denote

\[ n_{eq}(\rho, T) = 1.64(3)T + 1.132(12)\rho - 0.087(108). \]

\[ n_{eq}(\rho, T) = 2.65(11)T - 0.12(1)T^{2} + 0.77(5)\rho + 0.014(2)\rho^{2} + 0.13(9) \] (right inset) and \( n_{eq}(\rho, T) = -0.000057(7)\rho^{2} + 0.083(4)\rho + 8.9(4) - 0.97(11)T \) (left inset).

(b): At low temperatures, the equilibrium occupancy plateaus at integer values (bottom), but the difference in lattice constant \( a = (\sqrt{2}n_{c}/\rho)^{1/3} \) between neighboring integer occupancy phases is too small to induce demixing (top). At \( T = 0 \), the lattice constant for \( \rho > \rho_{cp} \) is fixed and the occupancy increases linearly.

(c): Relative particle number fluctuation for various temperatures. The theoretical prediction for the fluctuations between \([n_{eq}^{\text{up}}]\) and \([n_{eq}^{\text{down}}]\) (solid line – see text) agree with the low temperature results.
FCC\((n_c)\). At \(T = 0\), however FCC\((n_c)\) with integer \(n_c \geq 2\) is again only stable at a single density \(\rho = n_c \rho_{cp}\), where \(\rho_{cp} = \sqrt{2}\) is the crystal close packing density of hard spheres. For \(n_c \rho_{cp} < \rho < (n_c + 1) \rho_{cp}\) the ground state is a random mixture of sites with occupancy \(n_c\) and \(n_c + 1\), because all cluster arrangements are degenerate (Fig.9.2(b)).

What about intermediate temperatures? In the GEM-4, transitions between cluster phases with different integer occupancy FCC\((n_c)\)–FCC\((n_c + 1)\) was found to become first order below an isotructural critical point [19]. Although a simple phonon analysis suggests that a similar type of transition may be possible in any cluster-forming system at low enough temperature [17], no such transition is observed here. This point deserves further consideration. For the small integer occupancy studied, a multiply-occupied lattice site is effectively a large coarse-grained particle whose size is related to the lattice constant \(a\). To obtain a first order isotructural transition, i.e., demixing of FCC\((n_c)\) and FCC\((n_c + 1)\) phases, a large enough size heterogeneity between sites of different occupancy is necessary for the free volume gained to overcome the entropy of mixing, as in binary hard sphere mixtures [239]. Otherwise, the sites with occupancy \(n_c\) and \(n_c + 1\) randomly mix. For the PSM, the evolution of the lattice constant in Fig. 9.2(b) indicates that the largest lattice difference between FCC(1) and FCC(2) is smaller than 3\% at \(T = 0.05\). Because this difference goes to zero at \(T = 0\), its relatively rapid shrinking with \(T\) may be sufficient to prevent isostructural phase separations, although it cannot be excluded altogether. This qualitative distinction between the GEM-4 and the PSM reflects the sensitive dependence of isostructural transitions on the details and convexity of the interaction potential [240]. The relatively long tail of the GEM-4 interaction indeed results in an additional energetic contribution to the lattice constant, and overcomes the entropy of mixing at low enough \(T\) (Sec. 8.2). For GEM-\(n\) with \(4 < n < \infty\), one expects the threshold lattice constant difference between lattices with occupancy \(n_c\)
and $n_c + 1$ to also depend on $T$ via the entropy of mixing. Qualitatively, we expect the isostructural critical point to steadily decrease with the increase of $n$ and $n_c$. A better knowledge of the drive for binary hard sphere mixtures of different size ratios to demix would be needed to estimate the equivalent behavior in the GEM-$n$.

With the equilibrium occupancy at hand, we study how the number of particles on a given site fluctuates in various $T$ regimes. This quantity is particularly important in determining which of the basic theoretical approximation is most analytically reasonable. Overall the relative fluctuation decreases with increasing temperature and density, but this progression is not monotonic (Fig. 9.2 Right). At low temperatures ($T < 0.1$), a system with an equilibrium occupancy intermediate between two integers $\lfloor n_{eq}^c \rfloor < n_{eq}^c < \lceil n_{eq}^c \rceil$ can be seen as a random mixture of sites with occupancy $\lfloor n_{eq}^c \rfloor$ and occupancy $\lceil n_{eq}^c \rceil$. Excitations creating $\lceil n_{eq}^c \rceil + 1$ or $\lfloor n_{eq}^c \rfloor - 1$ defects are strongly suppressed. In that limit, the problem can be solved analytically. The probability of a site having $\lfloor n_{eq}^c \rfloor$ $(\lceil n_{eq}^c \rceil)$ particles is $n_{eq}^c - \lfloor n_{eq}^c \rfloor$ $(\lceil n_{eq}^c \rceil - n_{eq}^c)$, and the resulting variance is $\sigma_{n_c}^2 = (2\lfloor n_{eq}^c \rfloor + 1) n_{eq}^c - \lfloor n_{eq}^c \rfloor \lceil n_{eq}^c \rceil - (n_{eq}^c)^2$. The $T = 0.05$ results agree very well with this approximation (Fig. 9.2(c)). This behavior explains why the mean-field cell model works increasingly well with decreasing $T$ and nearly quantitatively for $T \lesssim 0.03$. As temperature increases, fluctuations become more pronounced, and vary continuously with occupancy. In this limit the crystal behavior is better approximated by a DFT-type treatment in which the free energy is optimized with respect to occupancy and fluctuations, assuming a Gaussian distribution [22].

As determined in earlier studies [15, 19], the bulk modulus of cluster crystals, once decomposed into its two constituents (Chapter 3), shows a strong softening correction due to the creation/annihilation process of lattice sites at high temperatures (Fig. 9.3). But in the integer occupancy regime, such as at $T = 0.05$ for $\rho = 2.4$, the virial part is the full resistance to external compression [19]. The two contributions to the coefficient of thermal expansion can be similarly calculated. At $T = 4$ and
Figure 9.3: The bulk modulus $B$ and its virial contribution $B_{\text{vir}}$ at $T = 4$ and $T = 0.05$ (inset). The virial part $B_{\text{vir}}$ is significantly softened by the cluster contribution, except in the low $T$ plateau regime ($\rho = 2.4$).

Table 9.1: Calculation of $\alpha$ at $T = 4.0$ and $p = 206$ with $n_{\text{c}}^{\text{eq}} = 19.77$ using (a1) a fit of the $T = 3.0-5.0$ results (Fig. 9.2), (a2) multiple $NpT$ simulations with $n_{\text{c}} = 19.77$, (a3) multiple $NpT$ simulations with $n_{\text{c}}^{\text{eq}}$ determined in (a1), (b1) histogram reweighting (Fig. 5.7), (b2) histogram reweighting (Eq. 5.82), (c) a direct $[N]pT$ simulation (Eq. 5.78), and (d) the fluctuation identity (Eq. 3.33).

<table>
<thead>
<tr>
<th>$\alpha$</th>
<th>$\alpha_{\text{vir}}$</th>
<th>$\left(\frac{\partial n_{\text{c}}^{\text{eq}}}{\partial T}\right)_{\text{vir}}$</th>
<th>$\frac{1}{v} \left(\frac{\partial v}{\partial n_{\text{c}}^{\text{eq}}}\right)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.195(10)$^{a1}$</td>
<td>0.169(10)$^{a2}$</td>
<td>-0.97(10)$^{a1}$</td>
<td></td>
</tr>
<tr>
<td>0.202(10)$^{b1+b2+c}$</td>
<td>0.170(10)$^{b2}$</td>
<td>-1.22(10)$^{b1}$</td>
<td>-0.0265(3)$^c$</td>
</tr>
<tr>
<td>0.168(10)$^d$</td>
<td></td>
<td></td>
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</tr>
</tbody>
</table>

$p = 206$, for instance, calculations of the different components of Eq. 3.11 agree with each other and with the decomposition (Table 9.1).

9.3 PSM Phase Diagram

The fluid-crystal transition, which is the only phase transition in the PSM, is extracted from the equilibrium free energies of both phases. The high and low $T$ regimes are treated separately, because the underlying physics is markedly different above and below the onset of clustering at coexistence around $T \sim 0.1$. 

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At high $T$, the coexistence regime on the $T$-$\rho$ phase diagram and the coexistence pressure on the $p$-$T$ phase diagram decreases smoothly towards $T \sim 0.1$. At melting $n_c^{eq}(\rho_{coex})$ increases roughly linearly with $T$, because the coexistence density itself increases roughly linearly with $T$, as discussed above (Fig. 9.4). DFT results capture the transition relatively well for $T \geq 3$, but strongly deviate below that point [22].

Yet attributing the deviation to a stronger hard-sphere character below that $T$ [22], is not supported by the numerical results, so another physical assumption of the theory may then be breaking down.

For $T \lesssim 0.1$ at coexistence, two conflicting descriptions have previously been suggested (Fig. 9.4). First, a mixed DFT (fluid) and cell theory (crystal) study
predicted that the fluid-solid transition continuously approaches the HS limit upon lowering $T$ [20]. Although the solid free energy was found to be indistinguishable from the HS results at finite temperatures, changes to the fluid phase resulted in a steady drift away from the HS behavior for $T > 0$. Second, a full DFT treatment predicted a crossover temperature from a HS-like coexistence to a different regime around $T = 0.35$ [21]. We find the second scenario to be qualitatively correct, although its predicted crossover temperature is nearly three times larger than the numerically determined one. For $T \sim 0.1$, the coexistence crystal density gets smaller than the HS close packing density $\rho_{cp} = \sqrt{2}$. Clustering then gets suppressed and the fluid-solid coexistence curve is inflected. Below $T < 0.07$, the fluid coexists with an essentially singly-occupied FCC phase. The transition is hard sphere-like with the corresponding coexistence pressure and densities (Fig. 9.4).

That there should be a crossover can physically be understood from the fact that at $T \ll 1$ particle overlaps are rare and uncorrelated. They therefore marginally stabilize both the fluid and crystal phases in a similar way. Once the concentration of overlaps becomes sufficiently high, however, the difference in structure between the ordered and disordered phases matters. This distinction between the high and low $T$ regime also has a dynamical signature [241, 242]. Collisions between particles can be divided in two types: soft refractive collisions, in which a particle goes through another, and hard reflective collisions, in which particles elastically bounce back from each other. At temperatures $T \lesssim 0.3$ from molecular dynamics simulations [242] or $T \lesssim 0.25 - 0.5$ from an Enskog-type theoretical analysis [241], the first collision type is highly suppressed because the particle momenta are low, and the collision frequency of the second type is as high as in hard spheres.

Unlike for the GEM-4 model, where first-order phase transitions between integer-occupancy lattices are observed at low $T$, crystal lattice occupancy in the PSM changes continuously. The stability regime of integer-occupancy phases, such as
FCC2 and FCC3, only occupies a narrow slice of the phase diagram at low temperatures. Above $T \sim 0.1$, these phases join the continuum of non-integer-occupancy crystals whose $T$-$\rho$ stability regime is but a line that extends smoothly up to the liquid-solid coexistence boundary. The cell model fails to capture this regime’s behavior (Fig. 9.4). It notably erroneously predict the existence of an intermediate single-double-triple occupancy regime (* in Fig. 9.4). The limited extent of occupancy fluctuations at this low $T$ (Fig. 9.2(c)) shows that such high-energy excitations are unphysical. Simulations indeed clearly delineate the single-double from the double-triple occupancy regimes.

9.4 Conclusion

In this chapter, we have efficiently applied the $[N]pT$ simulation and thermodynamic integration to determine the phase diagram of the canonical penetrable sphere model, which forms cluster crystals at high densities. The $[N]pT$ ensemble approach naturally allows for histogram reweighting, which was here used to calculate the response functions.

The resulting formalism and method are analogous to a constant pressure version of the approach used for determining the binary hard sphere mixture phase diagram [239, 243], which it should be able to calculate with some adjustments. The approach also allows for the study of models that form crystals in which the vacancy concentration is relatively large, such as hard cubes [244, 245]. The key limitation for these implementations is the need for an efficient particle insertion algorithm and a good initial guess of the conjugate field.
Appendix A

Virial Expression of Pressure

This appendix gives derivation of virial expression of pressure in various systems with singular/discontinuous potential. Recall the virial is defined as $W = - \sum_{i<j} w(r_{ij})$, where $w(r) = r \frac{du(r)}{dr}$.

The pressure is

$$p = \rho k_B T + \frac{\langle W \rangle}{3V},$$  \hspace{1cm} (A.1)$$

and in an isotropic system with radial distribution $g(r)$

$$p = \rho k_B T - \frac{\rho^2}{6} \int r \cdot \nabla u(r) g(r) dr$$

$$= \rho k_B T - \frac{\rho^2}{6} \int r \frac{du(r)}{dr} g(r) 4\pi r^2 sr$$

$$= \rho k_B T - \frac{2\pi \rho^2}{3} \int \frac{du(r)}{dr} g(r) r^3 dr$$

$$= \rho k_B T + \frac{2\pi \rho^2 k_B T}{3} \int_0^\infty \frac{de^{-\beta u(r)}}{dr} y(r) r^3 dr.$$

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The last equality is based on the arrangement factoring a continuous function $y(r)$ out of $g(r)$

$$g(r) = y(r)e^{-\beta u(r)}, \quad (A.3)$$

which leads to

$$g(r)\frac{du(r)}{dr} = -k_B Ty(r)\frac{de^{-\beta u(r)}}{dr}. \quad (A.4)$$

Let $\lim_{r \to r_0^+} g(r) = g_+(r_0)$ and $\lim_{r \to r_0^-} g(r) = g_-(r_0)$ be the upper and lower limits of $g(r)$ at $r_0$.

A.1 Hard Sphere (HS)

For HS, $e^{-\beta u(r)} = H(r - \sigma)$, where the Heaviside step function

$$H(r - \sigma) = \begin{cases} 0, & r < \sigma \\ 1, & r > \sigma \end{cases}, \quad (A.5)$$

and its derivative is the Dirac delta function

$$\frac{dH(r - \sigma)}{dr} = \delta(r - \sigma). \quad (A.6)$$

So

$$p_{HS} = \rho k_B T + \frac{2\pi \rho^2 k_B T}{3} \int_0^\infty \delta(r - \sigma)y(r)r^3dr$$

$$= \rho k_B T + \frac{2\pi \rho^2 k_B T}{3} \sigma^3 y(\sigma)$$

$$= \rho k_B T + \frac{2\pi \rho^2 k_B T}{3} \sigma^3 g_+(\sigma) \quad (A.7)$$
A.2 Penetrable Sphere Model (PSM)

For the PSM, \( e^{-\beta u(r)} = e^{-\beta \epsilon} H(\sigma - r) + H(r - \sigma) \), so

\[
p_{\text{PSM}} = \rho k_B T + \frac{2\pi \rho^2 k_B T}{3} \int_0^\infty \left[ -e^{-\beta \epsilon} \delta(r - \sigma) + \delta(r - \sigma) \right] y(r)r^3 dr
\]

\[
= \rho k_B T + \frac{2\pi \rho^2 k_B T}{3} \left[ -e^{-\beta \epsilon} y(\sigma)\sigma^3 + y(\sigma)\sigma^3 \right]
\]

\[
= \rho k_B T + \frac{2\pi \rho^2 k_B T}{3} \sigma^3 \left[ g_+(\sigma) - g_-(\sigma) \right].
\]  \(\text{(A.8)}\)

A.3 Square Well (SW)

For the SW,

\[
e^{-\beta u(r)} = \begin{cases} 0 & , \quad r < \sigma \\ e^{-\beta \epsilon} & , \quad \sigma < r < \lambda \sigma \\ 1 & , \quad r > \lambda \sigma \end{cases}
\]  \(\text{(A.9)}\)

which can be decomposed into the form \( e^{-\beta u(r)} = e^{-\beta \epsilon} H(r - \sigma) - e^{-\beta \epsilon} H(r - \lambda \sigma) + H(r - \lambda \sigma) \), so

\[
p_{\text{SW}} = \rho k_B T + \frac{2\pi \rho^2 k_B T}{3} \int_0^\infty \left[ e^{-\beta \epsilon} \delta(r - \sigma) - e^{-\beta \epsilon} \delta(r - \lambda \sigma) + \delta(r - \lambda \sigma) \right] y(r)r^3 dr
\]

\[
= \rho k_B T + \frac{2\pi \rho^2 k_B T}{3} \left[ e^{-\beta \epsilon} y(\sigma)\sigma^3 - e^{-\beta \epsilon} y(\lambda \sigma)\lambda^3 \sigma^3 + y(\lambda \sigma)\lambda^3 \sigma^3 \right]
\]

\[
= \rho k_B T + \frac{2\pi \rho^2 k_B T}{3} \sigma^3 \left[ g_+(\sigma) - \lambda^3 \sigma^3 g_-(\lambda \sigma) + \lambda^3 \sigma^3 g_+(\lambda \sigma) \right].
\]  \(\text{(A.10)}\)
Appendix B

Mean-Field Theory of the IC Model

This appendix provides detailed derivations of the mean-field theory in Ref [7]. For the lattice Fourier transform method, one can refer to Refs. [65] and [157].

B.1 Fourier Transform of the Hamiltonian $H_{IC}$

\[
H_{IC} = \frac{J}{2} \sum_i \sum_j \frac{1}{N} \sum_k \hat{V}(k)e^{-ik(r_i-r_j)} \frac{1}{\sqrt{N}} \sum_{k'} \hat{S}(k')e^{-ik'r_i} \frac{1}{\sqrt{N}} \sum_{k''} \hat{S}(k'')e^{-ik''r_j}
\]

\[
= \frac{J}{2 N^2} \sum_k \sum_{k'} \sum_{k''} \hat{V}(k)\hat{S}(k')\hat{S}(k'') \sum_i e^{-i(k+k')r_i} \sum_j e^{i(k-k'')r_j}
\]

\[
= \frac{J}{2} \sum_k \sum_{k'} \sum_{k''} \hat{V}(k)\hat{S}(k')\hat{S}(k'')\delta(k+k')\delta(k-k'')
\]

\[
= \frac{J}{2} \sum_k \hat{V}(k)\hat{S}(-k)\hat{S}(k)
\]

\[
= \frac{J}{2} \sum_k \hat{V}(k) |\hat{S}(k)|^2.
\]

(B.1)
B.2 Fourier Transform of the Ising Part $H_I$

\[ H_I = -\frac{J}{2} \sum_i s_i \sum_{\Delta_i \in NN} s_{\Delta_i} \]

\[ = -\frac{J}{2} \sum_i \left[ \frac{1}{\sqrt{N}} \sum_k \hat{S}(k) e^{-ik \cdot r_i} \right] \sum_{\Delta_i \in NN} \left[ \frac{1}{\sqrt{N}} \sum_k \hat{S}(k) e^{-ik \cdot r_{\Delta_i}} \right] \]

\[ = -\frac{J}{2N} \sum_i \left[ \sum_k \hat{S}(k) e^{-ik \cdot r_i} \right] \sum_{\Delta_i \in NN} \left[ \sum_k \hat{S}(k) e^{-ik \cdot (r_i + \Delta_r)} \right] \]

\[ = -\frac{J}{2N} \sum_k \sum_{k'} \hat{S}(k) \hat{S}(k') \sum_i e^{-i(k+k') \cdot r_i} \sum_{\Delta_r} e^{-i k' \cdot \Delta_r} \]

\[ = -\frac{J}{2N} \sum_k \sum_{k'} \hat{S}(k) \hat{S}(-k') N \delta(k + k') \sum_{\Delta_r} e^{-i k' \cdot \Delta_r} \]

\[ = -\frac{J}{2} \sum_k \hat{S}(k) \hat{S}(-k) \sum_{\Delta_r} e^{i k \cdot \Delta_r} \]

\[ = -\frac{J}{2} \sum_k \hat{S}(k) \hat{S}(-k)(e^{ik_x} + e^{-ik_x} + e^{ik_y} + e^{-ik_y} + e^{ik_z} + e^{-ik_z}) \]

\[ = -J \sum_k |\hat{S}(k)|^2 (\cos k_x + \cos k_y + \cos k_z) \]

\[ = -J \sum_k \sum_{\alpha=x,y,z} \cos k_{\alpha} |\hat{S}(k)|^2. \]

Here \( \Delta r = (\pm 1, 0, 0), (0, \pm 1, 0), (0, 0, \pm 1) \) are the six nearest-neighbor (NN) position vectors in the simple cubic lattice.

B.3 Fourier Transform of the Coulomb Part $H_C$

First, let us prove the lattice Green’s function form

\[ v(r) = \frac{1}{|r|} = \frac{4\pi}{N} \sum_k \frac{e^{-ikr}}{2 \sum_{\alpha} (1 - \cos k_{\alpha})}. \] (B.3)
We know from electrostatics that the solution to the Poisson's equation

\[ \nabla^2 u(r) = -\rho(r) \]  

(B.4)

for a spherical domain is

\[ u(r) = \int \frac{\rho(r')}{4\pi|r - r'|} d^3r'. \]  

(B.5)

On a discrete lattice, the local charge density

\[ \rho(r) = \sum_{i=1}^{N} s_i \delta(r - r_i), \]  

(B.6)

and the potential

\[ u(r) = \sum_{i=1}^{N} \frac{s_i}{4\pi|r - r_i|}, \]  

(B.7)

gives a lattice version of the Poisson's equation

\[ \nabla^2 u(r) = \sum_{\Delta r} [u(r + \Delta r) - u(r)] = -\sum_{i=1}^{N} s_i \delta(r - r_i), \]  

(B.8)

whose eigen equation is

\[ \sum_{\Delta r} [\phi(r + \Delta r) - \phi(r)] = -\lambda \phi(r). \]  

(B.9)

Guessing a solution of the form \( \phi(r) = e^{-i\mathbf{k} \cdot \mathbf{r}} \), we find that the eigenfunctions and eigenvalues are

\[ \phi_k(r) = e^{-i\mathbf{k} \cdot \mathbf{r}}, \]  

(B.10)

\[ \lambda_k = 2 \sum_{\alpha=x,y,z} (1 - \cos k_\alpha), \]  

(B.11)

under the orthogonality condition

\[ \sum_r \phi_k(r)\phi_{k'}(r) = \sum_r e^{-i(k-k') \cdot r} = N \delta(k - k'). \]  

(B.12)
Seeking a solution in terms of eigen function expansion, i.e. substituting \( u(r) = \sum_k c_k \phi_k(r) \) into Eq. B.8, we get

\[
\sum_k c_k \nabla^2 \phi_k(r) = -\sum_k c_k \lambda_k \phi_k(r) = -\sum_{i=1}^N s_i \delta(r - r_i). \tag{B.13}
\]

Multiplying both sides by \( \phi_k^*(r) \) and summing over \( r \), we get from the orthogonality condition that

\[
\sum_k c_k \lambda_k N \delta(k - k') = \sum_{r, i=1}^N s_i \delta(r - r_i) e^{ik' \cdot r}, \tag{B.14}
\]

thus

\[
c_{k'} = \frac{\sum_r \sum_{i=1}^N s_i \delta(r - r_i) e^{ik' \cdot r}}{\lambda_{k'} N} = \frac{\sum_{i=1}^N s_i e^{ik' \cdot r_i}}{\lambda_{k'} N}, \tag{B.15}
\]

and,

\[
u(r) = \sum_k \frac{\sum_{i=1}^N s_i e^{ik \cdot r_i}}{\lambda_k N} e^{-ik \cdot r} = \sum_{i=1}^N s_i \sum_k \frac{e^{-ik \cdot (r - r_i)}}{\lambda_k N}. \tag{B.16}
\]

Comparing above result with Eq. B.7, we obtain

\[
\frac{1}{4\pi |r - r_i|} = \sum_k \frac{e^{-ik \cdot (r - r_i)}}{\lambda_k N}, \tag{B.17}
\]

which is Eq. B.3.

Second, we write

\[
H_C = \frac{Q}{2} \sum_{i \neq j} \frac{s_i s_j}{r_{ij}} = \frac{Q}{2} \sum_{i,j} v(r_{ij}) s_i s_j - \frac{Q}{2} \sum_{i=1}^Q v(0) s_i s_j, \tag{B.18}
\]

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where \( v(0) = 0.25273100986 \), as obtained from Eq. B.3. The first term

\[
I = \frac{Q}{2} \sum_{i,j} \frac{4\pi}{N} \sum_k \frac{e^{-ik'r_{ij}}}{2\sum_\alpha (1 - \cos k\alpha)} \frac{1}{\sqrt{N}} \sum_{k'} \hat{S}(k')e^{-ik'r_i} \frac{1}{\sqrt{N}} \sum_{k''} \hat{S}(k'')e^{-ik''r_j}
\]

\[
= \frac{Q}{2} \frac{4\pi}{N^2} \sum_k \sum_{k'} \sum_{k''} \frac{\hat{S}(k')\hat{S}(k'')}{2\sum_\alpha (1 - \cos k\alpha)} \sum_{i,j} e^{-ik'(r_i - r_j)} e^{-ik'r_i} e^{-ik''r_j}
\]

\[
= \frac{Q}{2} \frac{4\pi}{N^2} \sum_k \sum_{k'} \sum_{k''} \frac{\hat{S}(k')\hat{S}(k'')}{2\sum_\alpha (1 - \cos k\alpha)} \sum_i e^{-i(k + k')r_i} \sum_j e^{i(k - k'')r_j}
\]

\[
= \frac{Q}{2} \frac{4\pi}{N^2} \sum_k \sum_{k'} \sum_{k''} \frac{\hat{S}(k')\hat{S}(k'')}{2\sum_\alpha (1 - \cos k\alpha)} \delta(k + k') \delta(k - k'')
\]

\[
= \frac{Q}{2} \frac{4\pi}{N^2} \sum_k \frac{\hat{S}(-k)\hat{S}(k)}{2\sum_\alpha (1 - \cos k\alpha)}
\]

\[
= \frac{Q}{2} \frac{4\pi}{N^2} \sum_k \frac{|\hat{S}(k)|^2}{2\sum_\alpha (1 - \cos k\alpha)}.
\]

(B.19)

and the second term is

\[
II = \frac{Q}{2} v(0) \sum_i |s_i|^2 = \frac{Q}{2} v(0) N = \frac{Q}{2} v(0) \sum_k |\hat{S}(k)|^2.
\]

(B.20)

Therefore,

\[
H_C = \frac{Q}{2} \left[ 4\pi \sum_k \frac{|\hat{S}(k)|^2}{2\sum_\alpha (1 - \cos k\alpha)} - v(0) \sum_k |\hat{S}(k)|^2 \right].
\]

(B.21)

B.4 Fourier Transform of Mean-Field Equations

For the effective field

\[
\Delta H_i = -J \sum_j V_{ij} \langle s_j \rangle,
\]

(B.22)
we Fourier transform both sides to obtain

$$\frac{1}{\sqrt{N}} \sum_i e^{ik \cdot r_i} \sum_j \left[ \Delta H_i = -J \sum_j V_{ij} \langle s_j \rangle \right], \quad (B.23)$$

$$\frac{1}{\sqrt{N}} \sum_i \Delta H_i e^{ik \cdot r_i} \sum_j 1 = -J \sum_i e^{i(k \cdot (r_i + r_j - r_j))} \sum_j V_{ij} \frac{1}{\sqrt{N}} \sum_j \langle s_j \rangle, \quad (B.24)$$

$$\frac{1}{\sqrt{N}} \sum_i \Delta H_i e^{ik \cdot r_i} N = -J \sum_i \sum_j V_{ij} e^{i(k \cdot (r_i - r_j))} \frac{1}{\sqrt{N}} \sum_j \langle s_j \rangle e^{ik \cdot r_j}, \quad (B.25)$$

which gives the Fourier space effective field

$$\Delta \hat{H}(k) = -J \hat{V}(k) \hat{m}(k). \quad (B.26)$$

Similarly, multiplying both sides of the mean-field phase transition equation by

$$\frac{1}{\sqrt{N}} \sum_i e^{ik \cdot r_i},$$

$$k_B T_c \langle s_i \rangle = \Delta H_i, \quad (B.27)$$

leads to its Fourier transform

$$k_B T_c \hat{m}(k_c) = -J \hat{V}(k_c) \hat{m}(k_c). \quad (B.28)$$
Appendix C

Gauss-Lobatto Quadrature

To minimize the numerical error of the thermodynamic integration over parameter \( \lambda \), we use the Gauss-Lobatto Quadrature. To evaluate an integral

\[
I = \int_{-1}^{1} f(x) \, dx
\]

numerically, instead of choosing a few linearly distributed \( x_i \)'s and summing

\[
I = \sum_{i} f(x_i) \Delta x,
\]

the Gauss-Lobatto scheme uses an interpolation polynomial of order \( n \) to estimate the integral with \( n \) points \( x_i(i = 1, 2, \cdots, n) \) and the corresponding weight functions \( W(x_i) \) as

\[
I = \sum_{i=1}^{n} f(x_i)W(x_i).
\]  

(C.1)

For \( n \) integration points, the abscissa \( x_i \in [-1, 1] \) is the \((i-1)\)th zero of the Legendre polynomial derivative \( P'_{n-1}(x) \) and the weight

\[
W(x_i) = \frac{2}{n(n-1)[P_{n-1}(x_i)]^2},
\]  

(C.2)

which are available in standard mathematical function textbooks [189]. The integral can be well evaluated as long as \( f(x) \) is smooth along the path and \( n \) is large enough to capture the curve. To evaluate integrals over any interval \( y \in [a, b] \), one simply
transforms the variable keeping track of the Jacobian \(dy/dx\), and the integral is

\[
I = \int_{a}^{b} f(y)dy = \int_{-1}^{1} f(y(x)) \frac{dy}{dx} dx = \sum_{i=1}^{n} f(y_i) \left( \frac{dy}{dx} \right)_i W(x_i). \tag{C.3}
\]

Note that the transformation need not be linear. If \(y(x)\) is linear transformation, then

\[
y(x) = \frac{b - a}{2} x + \frac{b + a}{2}
\]

and the Jacobian is \((b - a)/2\).

For the thermodynamic integrations, we use following transformations with parameters \(A\), \(B\) and \(C\) to place \(\lambda\) more compactly in the rapid changing section of the integral curve ([0, 0.1] and [0.7, 1]).

For \(a = 0\) and \(b = 0.1\),

\[
y(x) = A \frac{x + 1}{2} 10^{\frac{x+1}{2}} - C, \tag{C.5}
\]

with \(A = 1, B - C = -1\).

For \(a = 1\) and \(b = 0.7\),

\[
y(x) = 1 - A \frac{x + 1}{2} 10^{\frac{x+1}{2}} - C, \tag{C.6}
\]

with \(A = 3, B - C = -1\).
In this appendix, we present an example of the cell list method written in C. As discussed in the text, one first needs to define the linked list `CellTrack[NumberOfParticles]`.

```c
struct LinkedList {
    int WhichCell;
    int Prev;
    int Next;
};

struct LinkedList CellTrack[NumberOfParticles];
int HeadOfChain[NumberOfCells];
```

At the beginning of the simulation, the cell list can be generated as

```c
for(i=0;i<NumberOfCells;i++)
    HeadOfChain[i]=-1;
for(i=0;i<NumberOfParticles;i++){
    CellTrack[i].WhichCell = CellDetermine(i);
    CellTrack[i].Next = HeadOfChain[CellTrack[i].WhichCell];
    if(CellTrack[i].Next != -1)
        CellTrack[CellTrack[i].Next].Prev = i;
    HeadOfChain[CellTrack[i].WhichCell] = i;
```
where the function `CellDetermine(i)` returns an integer indexing which cell particle
i belongs to.

During the simulation, when particles move in/out of cells, subroutines that
add/remove a particle into/from a cell are needed. To add a particle i into a cell
`iCell`, we can use

```c
void AddToCell(int i, int iCell)
{
    CellTrack[i].Next = HeadOfChain[iCell];
    if(CellTrack[i].Next!=-1)
        CellTrack[CellTrack[i].Next].Prev = i;
    HeadOfChain[iCell] = i;
    return;
}
```

while to remove a particle i from a cell `iCell`, we can use

```c
void RemoveFromCell(int i, int iCell)
{
    if(i == HeadOfChain[iCell]) // if i is the first in the cell
        HeadOfChain[iCell] = CellTrack[i].Next;
    else // i is NOT the first in the cell eg, ?? -> i -> ?? -> -1
        { CellTrack[CellTrack[i].Prev].Next = CellTrack[i].Next;
            if(CellTrack[i].Next != -1) // if i is not last in the cell
                CellTrack[CellTrack[i].Next].Prev = CellTrack[i].Prev;
        }
    return;
}
```

In order to calculate the energy, we can loop over particles using the cell list as

```c
for(i=0;i<NumberOfParticles;i++)
```

```c
}
```
\{ 
  iCell=CellTrack[i].WhichCell;
  for(cell=0;cell<NumberOfNeighborCells;cell++)
  { 
    jCell=NeighborCellList[iCell][cell];
    j=HeadOfChain[jCell]; // first particle in jCell
    while(j != -1) // not the last particle in jCell
    { 
      u += Potential(rij); // rij is distance between i and j
      j = CellTrack[j].Next; // next particle in the linked list
    }
  }
  u /= 2.0; // correct double counting

where the function Potential(rij) returns the potential energy of particles i and j at a distance of rij. The two dimensional array NeighborCellList[m][n] (n = 0, 1, ..., 26) stores the indices of the 27 cells that need to be considered for a particle in cell m.
Cluster Algorithm of the ANNNI Model

Close to the critical point, thermal fluctuations involve the correlated flipping of entire spin domains, which a traditional Monte Carlo single-spin flip algorithm cannot simulate the phenomenon efficiently. Cluster moves thus help accelerate the phase space sampling. In the original Wolff algorithm [177], the cluster is grown isotropically by adding neighboring spins of the same sign with a certain probability, the percolation probability, and the entire cluster is flipped under the requirement of microscopic reversibility. In systems of constant magnetization or occupation number, the exchange of two clusters of different signs must be used [246]. In an anisotropic system such as the ANNNI model, different percolation probabilities should be adopted when growing the cluster [2].

For Pleimling’s algorithm, it can be shown that $p_n = 1 - e^{-2\beta J}$ and $p_a = 1 - e^{-2\beta J_K}$ satisfy microscopic reversibility

$$\mathcal{N}(o)P_{\text{cluster}}(o)\text{acc}(o \rightarrow n) = \mathcal{N}(n)P_{\text{cluster}}(n)\text{acc}(n \rightarrow o),$$

(E.1)

with the probability of generating $n$ from $o$ equal to that of generating $o$ from $n$, i.e., $\text{acc}(o \rightarrow n) = \text{acc}(n \rightarrow o)$. Here $P_{\text{cluster}}(o)$ is the probability of growing the cluster.
Figure E.1: Number of all types of nearest neighbor interactions on the boundary of the cluster before and after spins are flipped. Next nearest neighbor interactions are analogous. Spins in boxes are in the cluster.

in the configuration \( o \). It is therefore equivalent to prove that

\[
\frac{P_{\text{cluster}}(o)}{P_{\text{cluster}}(n)} = \frac{N(n)}{N(o)} = e^{-\beta \Delta U},
\]

where \( \Delta U = U(n) - U(o) \). To complete the derivation, we introduce the following notation

- \( N \): number of \( \ominus-\ominus \) and \( \ominus-\oplus \) interactions inside the \( o \) or \( n \) cluster
- \( NN \): number of z-axial \( \ominus-\ominus-\ominus \) and \( \ominus-\ominus-\ominus \) interactions inside the \( o \) or \( n \) cluster
- \( n_1(n_2) \): number of \( \ominus-\oplus \) (or \( \ominus-\ominus \)) interactions across the boundary of the \( o \) cluster
- \( n_3(n_4) \): number of \( \ominus-\ominus \) (or \( \ominus-\ominus \)) interactions across the boundary of the \( o \) cluster
- \( nn_1(nn_2) \): number of \( \ominus-\ominus-\ominus \) (or \( \ominus-\ominus-\ominus \)) interactions across the z boundary of the \( o \) cluster
- \( nn_3(nn_4) \): number of \( \ominus-\ominus-\ominus \) (or \( \ominus-\ominus-\ominus \)) interactions across the z boundary of the \( o \) cluster.

When the cluster is flipped from \( o \) to \( n \), the number of different interaction types changes as shown in Fig. E.1, and therefore
\[
\frac{P_{\text{cluster}}(o)}{P_{\text{cluster}}(n)} = \frac{p_n^n (1 - p_n)^{n_3 + n_4} p_a^{NN} (1 - p_a)^{nn_1 + nn_2}}{p_n^n (1 - p_n)^{n_1 + n_2} p_a^{NN} (1 - p_a)^{nn_3 + nn_4}} = (1 - p_n)^{-\Delta n} (1 - p_a)^{\Delta nn}, \quad (E.3)
\]

where \(\Delta n = n_1 + n_2 - n_3 - n_4\) and \(\Delta nn = nn_1 + nn_2 - nn_3 - nn_4\). Recall that

\[
H_{\text{ANNNI}} = -J \sum_{\langle i,j \rangle} s_i s_j + \kappa J \sum_{[i,j]} s_i s_j, \quad (E.4)
\]

so the energy difference can be expressed as

\[
\Delta U_N = [-J(n_1 + n_2 - n_3 - n_4)] - [-J(-n_1 - n_2 + n_3 + n_4)] = -2J\Delta n, \quad (E.5)
\]
\[
\Delta U_{NN} = [J\kappa(nn_1 + nn_2 - nn_3 - nn_4)] - [J\kappa(-nn_1 - nn_2 + nn_3 + nn_4)] = 2J\kappa\Delta nn, \quad (E.6)
\]

and therefore

\[
\frac{\mathcal{N}(n)}{\mathcal{N}(o)} = e^{-\beta(\Delta U_N + \Delta U_{NN})} = e^{2\beta J\Delta n} e^{-2\beta J\kappa \Delta nn}. \quad (E.7)
\]

In order to satisfy

\[
(1 - p_n)^{-\Delta n} (1 - p_a)^{\Delta nn} = e^{2\beta J\Delta n} e^{-2\beta J\kappa \Delta nn}, \quad (E.8)
\]

we let \((1 - p_n)^{-\Delta n} = e^{2\beta J\Delta n}\) and \((1 - p_a)^{\Delta nn} = e^{-2\beta J\kappa \Delta nn}\), and substitute them into Eq. E.3. Microscopic reversibility is therefore proven

\[
\frac{P_{\text{cluster}}(o)}{P_{\text{cluster}}(n)} = e^{2\beta J\Delta n} e^{-2\beta J\kappa \Delta nn} = \frac{\mathcal{N}(n)}{\mathcal{N}(o)}. \quad (E.9)
\]
Appendix F

Microreversibility of the \([N]pT\) Particle Insertion/Removal

In the particle insertion/removal steps of the \([N]pT\) ensemble simulation, the acceptance ratios of the forward and backward moves between states \((N, V)\) and \((N \pm 1, V)\) satisfy the microreversibility condition

\[
\frac{\text{acc}(N \rightarrow N \pm 1, V)}{\text{acc}(N \pm 1 \rightarrow N, V)} = e^{\beta \Delta G^\pm} \eta^\pm e^{-\beta \Delta E^\pm} = e^{\beta \Delta G^\pm} \frac{Q(N \pm 1, V, T)}{Q(N, V, T)} \frac{P_{NV}(N \pm 1, V)}{P_{NV}(N, V)},
\]

\(\text{(F.1)}\)

\(\text{(F.2)}\)

\(\text{(F.3)}\)
i.e., at equilibrium they generate states satisfying the joint distribution $\mathcal{P}_{NV}(N, V)$.

The final resulting distribution of $N$ is therefore

$$\frac{\mathcal{P}_N(N+1)}{\mathcal{P}_N(N)} = \frac{\sum_V \mathcal{P}_{NV}(N+1, V)}{\sum_V \mathcal{P}_{NV}(N, V)}$$  \hspace{1cm} (F.4)

$$= e^{\beta \Delta G \pm} \frac{\sum_V e^{-\beta \nu V} Q(N+1, V, T)}{\sum_V e^{-\beta \nu V} Q(N, V, T)}$$  \hspace{1cm} (F.5)

$$= e^{\beta \tilde{G}_{N \pm 1}} \frac{\Delta(N \pm 1, p, T)}{\Delta(N, p, T)}.$$  \hspace{1cm} (F.6)

At convergence, $e^{\beta \tilde{G}_N \Delta(N, p, T)} = \text{constant}$, which indicates $\mathcal{P}_N(N \pm 1) \mathcal{P}_N(N) = 1$, i.e. $\mathcal{P}_N(N)$ is flat.
Appendix G

Logarithmic Summation in Histogram Reweighting

The histogram reweighting scheme often involves the summation of the form, e.g. $Q = \sum e^{-(\beta - \beta_0)E}$, whose exponential terms could be astronomically large or vanishingly small in large systems, if the reweighting temperature $\beta$ is not very close to the reference temperature $\beta_0$. In order to avoid this numerical overflow/underflow problem, one can use a logarithmic summation scale, which factors out the maximum exponential term before the sum [196]. In this appendix, we present an example of logarithmic summation in the reweighting of the histogram $H(V, E)$ over both pressure and temperature. The (partial) partition function at the reference point $\Delta(N, p_0, T_0)$ just equals to the number of samplings $M$. At a neighboring pressure $p$ and temperature $T$,

$$
\Delta(N, p, T) = \sum_V e^{-(\beta p - \beta_0 p_0)V} \sum_E \Omega(N, V, E) e^{-(\beta - \beta_0)E},
$$

(G.1)

and thermal quantities such as volume $V$ become

$$
\langle V \rangle = \frac{\sum_V V e^{-(\beta p - \beta_0 p_0)V} \sum_E \Omega(N, V, E) e^{-(\beta - \beta_0)E}}{\Delta(N, p, T)}.
$$

(G.2)
The C code to implement such a summation on logarithmic scale is as follows.

```c
#include <stdio.h>
#include <stdlib.h>
#include <math.h>
int i, NumberOfSamplings;
double T, T0, p, p0, beta, beta0;

// data input from the histogram
double V[NumberOfSamplings], E[NumberOfSamplings];
double Emin; // min E[i], can be negative
double SumlogD, logD[NumberOfSamplings], logDmax, logDmin;
double SumlogV, logV[NumberOfSamplings], logVmax, logVmin;
double SumlogE, logE[NumberOfSamplings], logEmax, logEmin;
double Volume, Energy;

SumlogD = 0.0;
SumlogV = 0.0;
SumlogE = 0.0;

logDmax = exp(-700.); // set maximum smallest possible
logDmin = exp(700.); // set minimum largest possible

logVmax = exp(-700.);
logVmin = exp(700.);

logEmax = exp(-700.);
logEmin = exp(700.);

for (i = 0; i < NumberOfSamplings; i++)
{
    // calculate logarithm of each term
    logD[i] = -(beta - beta0)*E[i] - (beta*p - beta0*p0)*V[i];
    if (logD[i] > logDmax) logDmax = logD[i]; // update maximum
    if (logD[i] < logDmin) logDmin = logD[i];
}
```
\[
\log V[i] = -(\beta - \beta_0)E[i] - (\beta p - \beta_0 p_0)V[i] + \log(V[i]);
\]
\[
\text{if}(\log V[i] > \log V_{\text{max}}) \log V_{\text{max}} = \log V[i];
\]
\[
\text{if}(\log V[i] < \log V_{\text{min}}) \log V_{\text{min}} = \log V[i];
\]

// in case energy can be negative, raise all energies by \(|\text{Emin}|+10\)
\[
\log E[i] = -(\beta - \beta_0)E[i] - (\beta p - \beta_0 p_0)\log V[i],
\]
\[
\quad \quad + \log(E[i]+\text{fabs}(\text{Emin})+10.0);
\]
\[
\text{if}(\log E[i] > \log E_{\text{max}}) \log E_{\text{max}} = \log E[i];
\]
\[
\text{if}(\log E[i] < \log E_{\text{min}}) \log E_{\text{min}} = \log E[i];
\]
\}

for(i=0;i<\text{NumberOfSamplings};i++)
{

// sum by factoring \(\exp(\log D_{\text{max}})\) out of each term
\[
\text{SumlogD} += \exp(\log D[i] - \log D_{\text{max}});
\]
\[
\text{SumlogV} += \exp(\log V[i] - \log V_{\text{max}});
\]
\[
\text{SumlogE} += \exp(\log E[i] - \log E_{\text{max}});
\]
\}

// add the maximum term back on log scale
\[
\text{SumlogD} = \log D_{\text{max}} + \log(\text{SumlogD});
\]
\[
\text{SumlogV} = \log V_{\text{max}} + \log(\text{SumlogV});
\]
\[
\text{SumlogE} = \log E_{\text{max}} + \log(\text{SumlogE});
\]
\[
\text{Volume} = \exp(\text{SumlogV} - \text{SumlogD}); \quad \text{// ensemble average}
\]
\[
\text{Energy} = \exp(\text{SumlogE} - \text{SumlogD}) - \text{fabs}(\text{Emin}) - 10.0; \quad \text{// correct } |\text{Emin}|+10
\]
Bibliography


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Biography

Kai Zhang was born on June 28th 1984, in Baoji (perhaps Hanzhong), Shaanxi, China. His father is an immigrant originated from Harqin, Liaoning, a mongol autonomous county in northeastern China. He grew up in Baoji until the age of sixteen. From 2000 to 2003, he attended the High School Affiliated to Shaanxi Normal University in Xi’an, Shaanxi. After that he spent four exciting and happy years at Tsinghua University, Beijing, China, where he got his B.S. in chemistry in 2007. In August 2007, he went to graduate school at Duke University, Durham, North Carolina, United States. He is to receive his Ph.D. in physical chemistry from Duke University in the summer of 2012.

Publications


