

## Competition between short-ranged attraction and short-ranged repulsion in crowded configurational space: A lattice model description

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We describe a simple nearest-neighbor Ising model that is capable of supporting a gas, liquid, and crystal, in characteristic relationship to each other. As the parameters of the model are varied, one obtains characteristic patterns of phase behavior reminiscent of continuum systems where the range of the interaction is varied. The model also possesses dynamical arrest, and although we have not studied it in detail, these “transitions” appear to have a reasonable relationship to the phases and their transitions.

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In many systems, one can observe a rich interplay between phase separation, critical phenomena, slowed dynamics, and solidification, the latter manifesting itself as both crystallization and glassification. These questions have a long and venerable past, but in modern condensed-matter theory the range of systems where the issues have become relevant [1–3] is remarkable. Recent interest in model systems extends from colloidal glasses [4], particle gels [3,5], polymeric gels [6], globular protein crystallization [7,8], and gellation. For example, it has recently transpired that even the simplest system with repulsive core and short-ranged attraction exhibits a large range of phase transitions, dynamical arrest (possibly with new dynamical logarithmic singularity [5,9]), and kinetic phenomena [10], the pertinent control parameter being the range of the attraction. So far it has not been possible to understand the inter-relation of all these effects. Such issues also lie at the heart of many important modern problems of materials science, including the formation of arrays of particles on optical wavelengths and knowledge-based materials design [11,12].

To fully explore these questions, we would need to describe an extended range of density, across a number of different phase boundaries, dealing naturally with criticality [13], metastability, and arrest phenomena [14], all in a coherent fashion, with tools that were applicable and reliable across these regimes. In the interim, progress can be made in various aspects of the problem [8,11,15].

The idea that the gas, liquid, crystal, and transitions between them can be studied within the same lattice model has been raised over the years in some interesting studies [16], and complex models have also been studied using such simple models [17]. However, there has never been any simple (lattice-based) general mechanism producing a liquid (considered as a large collection of attraction-dominated states with nearly degenerate energies) in an appropriate relation to gas and solid. Here, beginning from ideas introduced by Biroli and Mézard [18,19], we show that it is possible to caricature all the states, and their transitions, in a remarkably simple nearest-neighbor Ising model. In this model, dynamical arrest and glassy states are also naturally incorporated into the story.

In the model, space is divided into cubes of side  $a$ , characteristic of the particle size and the microscopic length of

the system. To the center of each cube we associate a site (coordination number  $c=6$ , in a tridimensional space) and Ising-like occupancy variable. Where a site is occupied, we define (respectively) attractive and repulsive interactions between  $c_a$  and  $c-r$ , of the nearest neighbors.

Thus  $c_r$  specifies the fraction of space within a given cube that is available to neighboring particles, given the nature of the repulsive interactions, while  $c_a$  specifies how many of those particles can benefit from the attractive energy of the system. While we emphasize that this is a caricature, rather than a representation, of the potential, we expect that  $c_r$  therefore expresses the complexity or irregularity of the core of the particle, reflected ultimately in the density at random close packing in the real system and in the model. The interpretation of  $c_a$  is more subtle. However, broadly speaking, a small number of ( $c_a$ ) attractive interactions are shared between a larger number ( $c_r$ ) of neighbors; there are many local configurations in which the attractive contribution saturates in the dense system. This freedom encourages the formation of a liquid. This idea is consistent with the rationale for the formation of a gel by short-ranged colloidal particles [1]. In that case, there is such limited freedom by which the attractions can be captured that the liquid arrests to form a gel-like state. There is also a general trend for the model to be dominated by the “liquid” state as we approach  $c_r=c_a=6$ , the nearest-neighbor model.

In our present study, we assume nearest-neighbor finite attractions ( $\epsilon$ ) and infinite repulsions, the latter to make contact with related studies [18,19].

Thus, the infinite repulsion between  $c_r$  neighbors may be written ( $0 \leq c_r \leq 6$ )

$$E_j^{\text{repulsive}} = \begin{cases} 0 & \text{if } l_j \leq c_r \\ +\infty & \text{if } l_j > c_r, \end{cases} \quad (1)$$

where  $l_j$  is the number of occupied nearest-neighbor sites. In the case of  $c_r=6$ , no repulsive interaction is present in the model. The attractive interaction is governed by the parameter  $c_a$  ( $0 \leq c_a \leq 6$ ) and is defined (per particle) as

$$E_j^{\text{attractive}} = \begin{cases} -l_j\epsilon & \text{if } l_j \leq c_a \\ -c_a\epsilon & \text{if } l_j > c_a, \end{cases} \quad (2)$$

where  $\epsilon > 0$  is the strength of the attraction. Throughout the paper we will define energies and chemical potential in units of  $k_B T$ , and the “effective” energy will refer to the combined exponent of energy and chemical potential in the partition function.

Despite the fact that this is a simple nearest-neighbor Ising model, it is remarkably rich and spatial frustration produces a large range of phenomena, some of which have previously been observed in more complicated lattice models. In such cases it has also been possible to formulate methods for their study [17,20–22]. For the present case we show that the existence of a liquid disposed between the gas and liquid, and the resulting triple point, originate in a large degeneracy of states that are found at zero temperature as “multiphase points.” In special cases we make the number of such states macroscopic, but even where they are not so, at finite temperatures we can cause the existence of an infinite number of near-degenerate states, and a liquid.

It is possible to determine the phase diagram of such models to a high degree of confidence. To begin with, we determine the ordered phases by construction of the zero-temperature states of the model. On the simple cubic lattice we rewrite the underlying effective Hamiltonian (itself a combination of pure energy and chemical potential) as a sum over octahedral fragments [22,23] with each of which we can associate an independent energy. We may then choose the “optimal” fragments that are able to tile the lattice, and thereby classify the zero-temperature states. There is at least one multiphase point [21–24] at which an infinity of zero-temperature states is degenerate, though the entropy per particle remains finite.

In general terms, the zero-temperature states are organized as follows. In three dimensions, there are 20 different types of fragment. Now, in the grand canonical ensemble, for fixed values of  $c_r$  and  $c_a$ , the energy of a particle-centered fragment has the form  $-q\epsilon - \mu$ , where  $\mu$  is the chemical potential and  $q$  is a positive integer number depending on the number of neighbors. All the vacancy-centered fragments have zero energy, unlike previous frustrated models. Therefore, we use a slightly different notation, defining as  $n$  and  $a$  the total number of nearest neighbors and the number of filled axes (linear triplets of sites, the extreme pair being occupied), respectively, and using a label  $p=0, 1$  on the left of the symbol of a fragment distinguishing the vacancy-centered and the particle-centered ones:  ${}_p f_n^a$ .

The internal energy per volume of a state of the model is given by

$$\frac{U}{L^3} = - \left( \sum_j^{\text{PC}} q_j \rho_j \right) \epsilon - \left( \sum_j^{\text{PC}} \rho_j \right) \mu, \quad (3)$$

where  $L^3$  is the lattice volume and  $\rho_j$  is the density of the  $j$ th fragment; the sum is intended only over the particle-centered fragment types (PC).

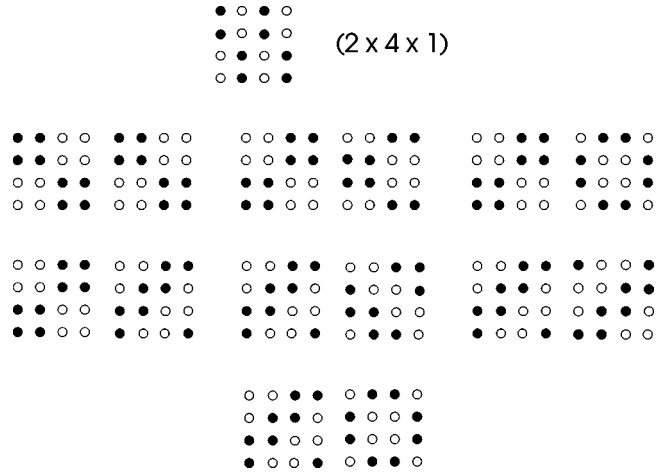


FIG. 1. Pure states for the case  $c_r=3, 4$ ,  $c_a=3$ . The first is made up of  $f_3^1$  fragments (top). There are seven pure phases made from the  $f_3^0$  fragments. Each of the seven pairs constitutes two layers of a  $4 \times 4 \times 4$  unit cell, the remainder being the particle-vacancy symmetric ones.

For  $\mu \rightarrow -\infty$ , the ground state is the zero-density gas, because in that limit the energy of every particle-centered fragment is infinite.

For  $\mu \rightarrow +\infty$ , the ground state is the most dense crystal, i.e., the crystal with the lowest density of vacancy-centered fragments. In between, we have many different situations, depending on the choice of  $c_a$  and  $c_r$ . Below we give only illustrative examples.

Thus, for the case  $c_a=3$  and  $c_r=3$  we have two fragments with energy  $-3\epsilon - \mu$ , but only one ( ${}_1 f_3^0$ ) tiles the space with the highest density vacancy-centered crystal  ${}_0 f_6^3$ . So there is one highest density crystal which is ordered along the diagonal with a repeat pattern of an occupied pair of layers and an unoccupied layer. This state is degenerate with the zero-density gas at the point  $\mu = -3\epsilon$ , the zero-temperature boundary between the gas and the crystal. There cannot be finite regions occupied by other states at zero temperature. In fact, a different state could have lower energy only if

$$q_{\text{PC}} = \frac{\sum_j^{\text{PC}} q_j \rho_j}{\sum_j^{\text{PC}} \rho_j} > 3 \quad (4)$$

and this is impossible because  $q_j \leq 3$  for every  $j$ .

The point  $\mu = -3\epsilon$  is a multiphase point, because two particle-centered fragments ( ${}_1 f_{3,1}^0, {}_1 f_3^1$ ) and every vacancy-centered fragment are degenerate. Some examples of crystals at the multiphase point are given in Fig. 1.

For  $c_a=4$  and  $c_r=3$ , there are two crystals with the highest energy 0.75, made up of the couples ( ${}_1 f_{4,0}^2, {}_1 f_6^3$ ), ( ${}_1 f_{4,0}^1, {}_1 f_6^3$ ), which are represented in Figs. 2(a) and 2(b), respectively.

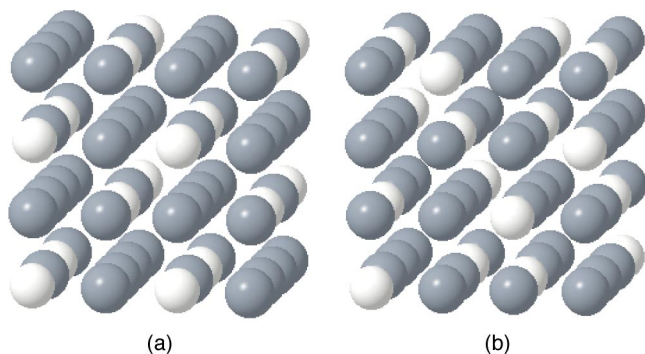


FIG. 2. Unit cells of the crystals at  $T=0$ . The black spheres represent an occupied position on the lattice and the white ones represent a vacancy. In both cases, the density is  $\rho=0.75$ . It transpires that the crystal (a) is more stable (at low finite temperature) than (b), and therefore only (a) is observed by cooling in the simulation.

The point  $\mu=-3\epsilon$  is still a multiphase point, but now *four* particle-centered fragments ( $f_{3,1}^0, f_{3,1}^1, f_{4,1}^1, f_{4,1}^2$ ) are degenerate. For this reason, here the multiphase point is much more degenerate.

Besides determining the low-temperature limit of the models, such considerations allow us to estimate, and thereby control, as a function of  $c_a$  and  $c_r$ , the number of low-temperature states where attraction is dominant. This allows us ultimately to fix the triple point of the system.

We present examples of grand canonical simulations ( $L=12, <10^6$  MCS). (We remark that we have as yet attempted no systematic exploration of dynamical arrest except the expected transient arrest phenomena of the underlying model [18].)

Phase diagrams for  $c_r=4, c_a=3$  and  $c_r=3, c_a=3$  are shown in Figs. 3 and 4, respectively.

The first is representative of a conventional gas-liquid-crystal phase diagram and the usual range of attractive interactions. Thus the simulations readily reproduce the zero-

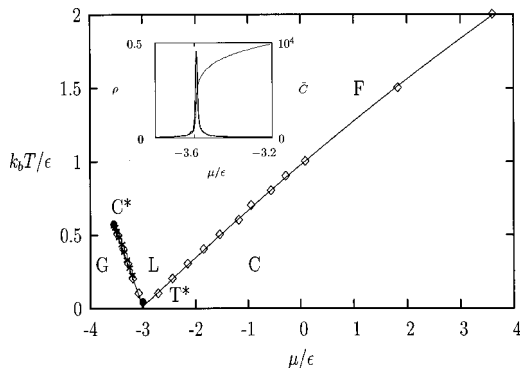


FIG. 3. Monte Carlo grand ensemble simulation for the case  $c_r=4, c_a=3$ . Graph of the temperature  $(\beta\epsilon)^{-1}$  vs chemical potential  $(\mu/\epsilon)$ . The (\*) are the results of the simulation lowering the temperature. The ( $\diamond$ ) are the results of the simulation increasing the chemical potential. The critical and triple point are labeled  $C^*$  and  $T^*$ , respectively. The inset shows an isothermal scan of density ( $\rho$ ) and heat capacity ( $\bar{C} \equiv C_V/k_B T$ ) for  $k_B T=0.6\epsilon$ .

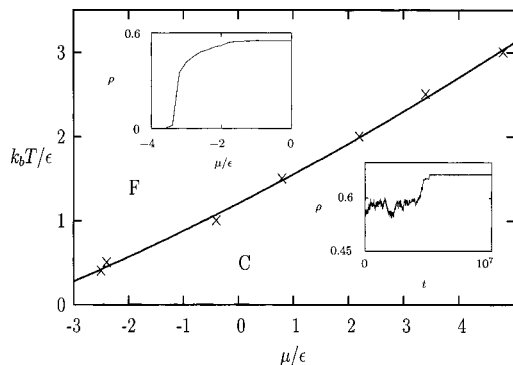


FIG. 4. Monte Carlo grand ensemble simulation for the case  $c_r=3, c_a=3$ . Graph of the temperature  $(\beta\epsilon)^{-1}$  vs chemical potential  $(\mu/\epsilon)$ . Upper inset: density vs chemical potential graph for  $k_B T=0.5\epsilon$ . Lower inset: long time behavior (density vs MC time steps) for the point at  $\mu=-2.4\epsilon$ .

temperature states of gas and crystal, and there is a significant range where the liquid state is present. In the inset to Fig. 3, we show the density and heat capacity in an isothermal cut of the phase diagram, just above the gas-liquid critical point. Such isotherms, as the temperature decreases from this point, exhibit an increasing peak height of the heat capacity, rising towards the critical point. The liquid-crystal phase boundary is a conventional first-order phase transition that asymptotes towards the fluid-repulsive crystal transition, as expected. Simulations near the (low but finite  $T$ ) triple point become quite slow.

The second phase diagram is chosen to show how the model represents a short-range potential. The simulations are still for quite small systems. However, the gas-liquid branch, if it exists, is so short to be almost unidentifiable. This would be the case, for example, of a continuum square-well potential when the well width is less than 10% of the core size.

Furthermore, it is intriguing to note the numerous other indications of a complex equilibrium, arrest, and kinetics picture, as expected for the equivalent continuum picture. In particular, there does appear to be a dense fluidlike state that is long lived, as well as a stringlike low-density fluid that may be credibly identified as a gel, both expected. (In the upper inset to the figure we show an isothermal scan in which the system makes an apparent transition to a dense liquidlike phase, whereas in the lower inset we show that this state degenerates to a crystal at very long times [7,8].)

In summary, we have shown that a very simple Ising lattice model, with only nearest-neighbor interactions, is capable of supporting all of the characteristic phenomena of particles with repulsive and attractive interactions (gas, liquid, crystals, and “glass-transition” phenomena of various kinds), and that variation of parameters provides a mechanism to mimic the range of the potential into important regimes that have yet to be understood.

Many of the outstanding problems of interest, such as metastability or buried critical points, arrest phenomena, and near criticality and gellation, are expected to be quite well-

described on lattices. Crystallization nuclei, and to some degree their growth are the most dubious aspects of a lattice description, but even there, many of the most difficult and subtle unexplained processes currently involve some element of near criticality [13], something which is well dealt with in the lattice, and is difficult to deal with in a useful manner otherwise.

Besides having a certain elegance in being the simplest

model known to exhibit all of the relevant phenomena, it seems likely that this model has considerable relevance to important practical issues.

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