

Structural aspects of the melting transition

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Assuming that their potential energy Φ is differentiable, arbitrary configurations for N particles in a container can be classified according to precursor mechanically stable packings. This is achieved in the multidimensional configuration space by following steepest descent paths on the Φ hypersurface downward to a local minimum. This "quenching" classification separates the many-body problem into two parts: (1) configurational packing statistics, and (2) thermal excitation within regions defined by the local Φ minima. This leads to the hypothesis that thermodynamic singularities associated with the first-order melting transition already appear in part (1). Computer studies of the melting transition in the two-dimensional Gaussian core system support that hypothesis. Examination of quenched configurations for this model system suggest new ways to describe the dense fluid (or liquid) state.

I. INTRODUCTION

One of the most prominent challenges for statistical mechanics continues to be the need to understand the melting transition. In spite of many valiant attempts a general solution remains beyond grasp. Now that molecular-level observation of melting events has become almost routine in digital computer simulations [1], important data is available on which a valid analytical theory probably could be based.

This paper presents a novel approach to describing order in liquids and solids, and to describing the transitions between those phases. We believe it will contribute significantly to eventual formulation of the desired universal melting theory.

Our general strategy is outlined in the next section. This is followed in Sec. III by its specific application to the two-dimensional Gaussian core model, a classical point-particle system whose properties are reasonably well understood [2-5]. We close in Sec. IV with a discussion of present results, with suggestions for further applications, and with predictions about the future development of this general viewpoint.

II. PARTITION FUNCTION TRANSFORMATIONS

We consider N molecules in a container of volume V . Both intermolecular and wall-molecule interactions (if any) will be included in the potential energy function ϕ . Although generalization is readily possible, we suppose for simplicity that the N molecules are identical structureless particles for which classical dynamics and statistical mechanics supply an appropriate description.

The classical partition function Z_N forms the basis for predicting thermodynamic properties. We have:

$$Z_N = \frac{1}{\lambda^{DN} N!} \int d\vec{r}_1 \dots \int d\vec{r}_N \exp(-\beta\phi) \quad (2.1)$$

Here λ is the mean thermal de Broglie wavelength, D is the space dimension, and β is $1/k_B T$ as usual.

Suppose that $\phi(\vec{r}_1 \dots \vec{r}_N)$ is bounded from below and is differentiable for all particle configurations $\vec{r}_1 \dots \vec{r}_N$ within V .

This potential function then can be used to divide the DN-dimensional configuration space for the many-body system into distinct regions $R(\alpha)$ which correspond respectively to the relative minima of ϕ in that space. Here we let α serve as an index for those minima. The procedure for this division is very simple; starting from any initial configuration $\vec{r}_1 \dots \vec{r}_N$ follow the path of steepest descent on the ϕ hypersurface until a minimum is encountered. Aside from a zero measure set of starting configurations (which can be disregarded), this assignment to minima is unique and exhaustive.

The connecting of initial arbitrary configurations to their respective minima amounts to a quenching operation. The steepest descent paths are solutions to the coupled first order differential equations

$$K \dot{\vec{r}}_i = -\vec{\nabla}_i \phi \quad (i = 1 \dots N) \quad (2.2)$$

where K is a positive constant whose precise value is irrelevant. If we imagine arresting at some specific moment the normal Newtonian dynamics

$$m \ddot{\vec{r}}_i = -\vec{\nabla}_i \phi \quad (i = 1 \dots N) \quad (2.3)$$

and switching over to evolution equation (2.2) thereafter, the system will automatically fall by steepest descent into that ϕ minimum for the region $R(\alpha)$ in which it finds itself at the switch-over. The end result configurationally is that which would physically be achieved by infinitely rapid quench toward absolute zero, since all inertial effects have been removed. Without inertia the N-body system is incapable of leaving $R(\alpha)$, since that would require climbing over a ridge-line on the ϕ hypersurface.

The next step is to rewrite Z_N in a way which isolates contributions from distinct regions $R(\alpha)$.

$$Z_N = \lambda^{-DN} \sum_{\alpha} \exp(-\beta\phi_{\alpha}) \int_{R(\alpha)} d\vec{r} \exp(-\beta\Delta_{\alpha}\phi) \quad (2.4)$$

Here ϕ is the value of ϕ at the minimum within $R(\alpha)$, and $\Delta_{\alpha}\phi$ is the potential measured from that minimum. The primed summation in Eq. (2.4) eliminates the redundancy that arises from particle permutation. There are always $N!$ equivalent minima and regions $R(\alpha)$ differing only by exchange, so it is necessary only to include one from each such equivalence class provided the $N!$ in Eq. (2.1) has been cancelled.

If the number N of molecules is large we can expect the number of ϕ minima (each of which represents a mechanically stable packing) to be enormous. In fact this latter number should increase exponentially with N . Consequently it makes sense to introduce a density $G(\phi_{\alpha})$ for the distribution of minima along the ϕ axis. Likewise it makes sense to introduce an average partition function for those $R(\alpha')$ whose minima fall in a narrow interval around any arbitrarily chosen ϕ_{α} . Thus we write:

$$\exp(-\beta F(\phi_{\alpha}, \beta)) = \langle \int_{R(\alpha')} d\vec{r} \exp(-\beta\Delta_{\alpha'}\phi) \rangle \quad (2.5)$$

It is reasonable to suppose that both $G^{1/N}$ and F/N can be treated as continuous and at least piecewise differentiable in the large system limit.

With these definitions we now have

$$Z_N = \lambda^{-DN} \int d\phi G(\phi) \exp(-\beta\phi - \beta F(\phi, \beta)); \quad (2.6)$$

it is no longer necessary to retain the index α . The partition function has been formally converted from a multiple configuration integral, Eq. (2.1), to a simple quadrature over potential energy. In any case of practical interest we can expect that $G(\phi)$ will differ from zero only over a finite ϕ interval between limits ϕ_{\min} and ϕ_{\max} that are essentially proportional to N .

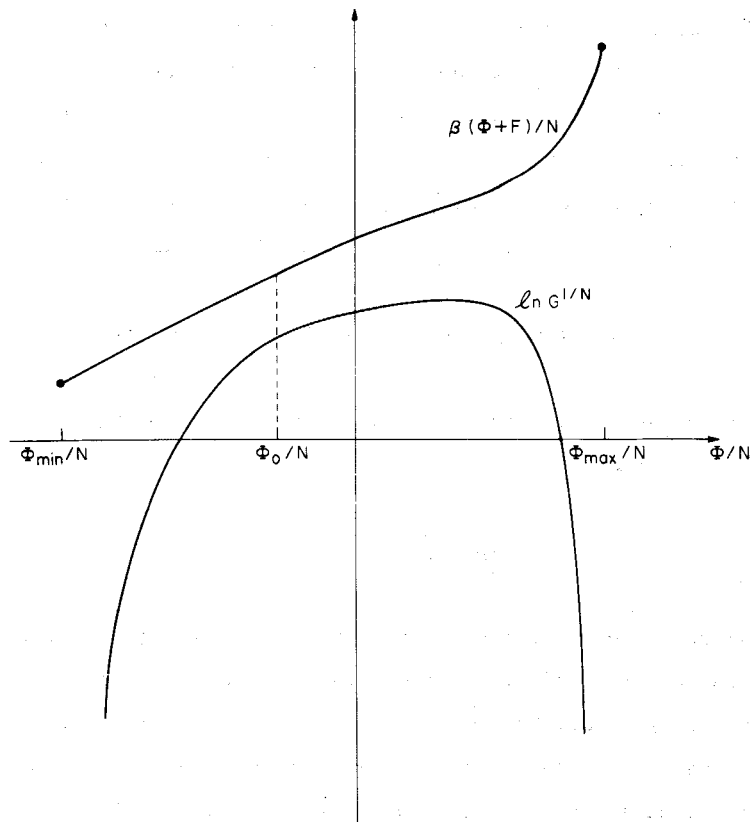


Figure 1. Graphical determination of $\Phi_0(\beta)$, the argument which maximizes the integrand in Eq. (2.6). The solution (vertical dotted line) occurs at the minimum upward separation from the $\ln G^{1/N}$ curve to the $\beta(\Phi+F)/N$ curve.

The integral in Eq. (2.6) can be evaluated by a maximum term method, at least in sufficient accuracy for prediction of thermodynamic properties. The corresponding graphical construction for $\phi_0(\beta)$, the value of the argument that maximizes the integrand, is illustrated schematically in Fig. 1. Separate curves are shown for $\ln G^{1/N}$ and for $\beta(\phi + F)/N$. The position of minimum upward displacement from the first curve to the second identifies ϕ_0 .

For any given system we ultimately require knowledge about the functions G , F , and ϕ_0 , and how they relate thermodynamically to the fluid-solid transition. It is also important to determine how molecular arrangements in any given thermodynamic state evolve to those in the corresponding quenched state. The following section begins to answer these questions for a specific model.

III. TWO-DIMENSIONAL GAUSSIAN CORE MODEL

The Gaussian core model is defined by the following pairwise-additive potential:

$$\phi = \sum \exp(-r_{ij}^2) \quad , \quad (3.1)$$

where appropriate reduced units for length and energy are used. This model has been the object of considerable study by analytical methods [2, 3, 6] and by computer simulation [7]. For present purposes we build upon a recent molecular dynamics investigation of this in two dimensions, employing $N = 780$ particles subject to periodic boundary conditions [4, 5]. This last feature renders unnecessary the inclusion of wall interactions in ϕ .

It has been determined that this system undergoes a first-order melting transition from a triangular (close-packed) crystal

to isotropic fluid. Exhaustive molecular dynamic calculations at the fixed value of the reduced density

$$\rho^* = 3^{-1/2} \quad (3.2)$$

show that melting causes the pressure to drop, i.e., the fluid is denser than the solid at fixed pressure. Because the coexisting fluid and solid have different densities the melting process at fixed density is spread over a finite temperature range. The computer simulation studies show this range to be approximately

$$6.6 \times 10^{-3} \leq T^* \leq 7.2 \times 10^{-3} \quad (3.3)$$

for the density in Eq. (3.2).

Several system configurations from the $\rho^* = 3^{-1/2}$ molecular dynamics have been selected and quenched according to the above procedure. These initial configurations came from a wide range of starting temperatures and included both crystalline and fluid states, as well as states within the coexistence region (3.3).

The triangular lattice phase shows thermal excitations that can be described simply as elastic waves. These are decoupled phonons at very low temperature but they become substantially anharmonic and coupled as the melting range (3.3) is approached from below. The equilibrium concentration expected for lattice defects (vacancies, interstitials, isolated dislocations) is apparently so low that they would not be expected to occur observably with the given system size over any reasonable computing time. Consequently the quench operation merely removes the elastic deformation and returns the system to the perfect lattice arrangement. The corresponding ϕ minimum is one of the equivalent absolute minima. At the given density the potential energy

on a per-particle basis at these minima is

$$\phi_{\min}/N = 0.414\ 453\ 166 \quad (3.4)$$

Quenches from fluid states or states of coexistence produce more interesting results. Figures 2 and 3 respectively present a fluid configuration ($T^* = 7.41 \times 10^{-3}$) and the quenched configuration produced therefrom. These pictures show the 780 particles classified according to the number of sides to their nearest neighbor. (Wigner-Seitz) polygons. Particles in hexagons appear as asterisks, while all others are shown as integers giving the number of polygon sides. In

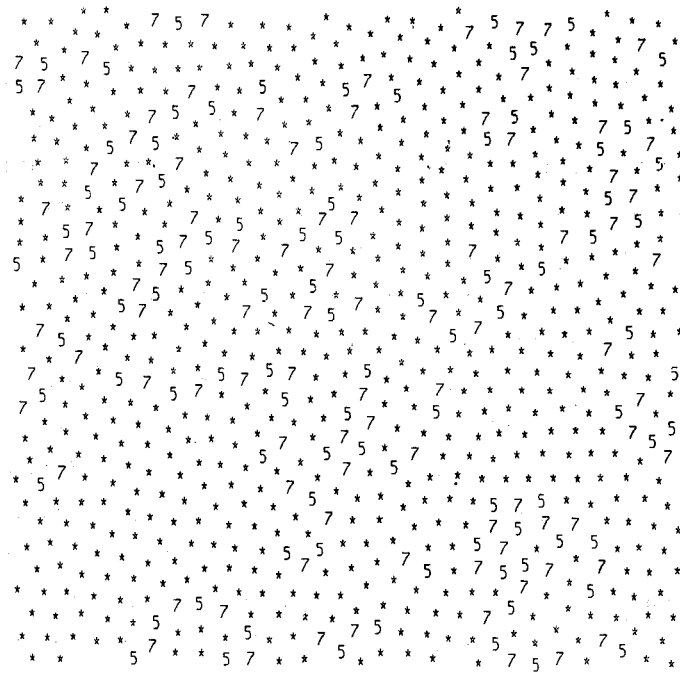


Figure 2. Particle configuration for the fluid phase of the two-dimensional Gaussian core model ($\rho^* = 3^{-1/2}$, $T^* = 7.41 \times 10^{-3}$). The 780 particles are classified by their nearest neighbor polygons. Particles with six nearest neighbors are shown as asterisk, others are shown as integers giving their numbers of nearest neighbors.

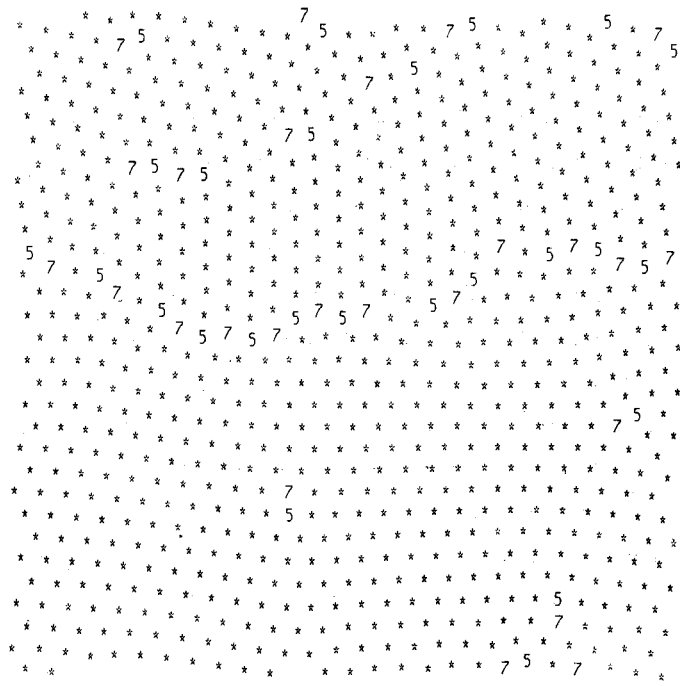


Figure 3. Constant-area quench of the configuration shown in Fig. 2. The system is mechanically stable: it resides at a local potential energy minimum.

the ordered crystal all particles inhabit hexagons, so that non-hexagonal particles locate structural disorder.

Comparison of Figs. 2 and 3 shows that quenching drastically simplifies the structural pattern. The disorganized texture of the unquenched system organizes into a polycrystalline mosaic with far fewer nonhexagonal particles. Note that isolated 5-7 pairs are dislocations, and a linear path of oriented dislocations constitutes a grain boundary whose angle depends on the dislocation spacing [8]. Figure 3 presents an obvious case of such a boundary running across the system.

From this quench example and others we have examined it is clear that the dense fluid amounts to a thermally excited polycrystal. Starting with the fluid state, quenching invariably produces vivid patterns that are hidden initially. The relative ϕ minima attained in fluid quenches lie above ϕ_{\min} owing to the remanent disorder of

grain boundaries and isolated dislocations. For the case illustrated in Figure 3, ϕ/N lies approximately 1.22×10^{-3} above ϕ_{\max}/N .

Experience shows that the mean grain size for the quenched packings depends upon the temperature of the starting state. Higher temperatures tend to produce smaller grains and larger grain boundary angles, and since this implies greater total disorder the greater will be the packing potential energy.

Figure 4 shows the mapping we have inferred thus far, as a function of starting temperature T^* , between the thermodynamic average potential energy per particle $\langle\phi\rangle/N$ and the mean value of the same quantity after quench, ϕ_0/N . This last quantity was the objective of the graphical construction illustrated in figure 1.

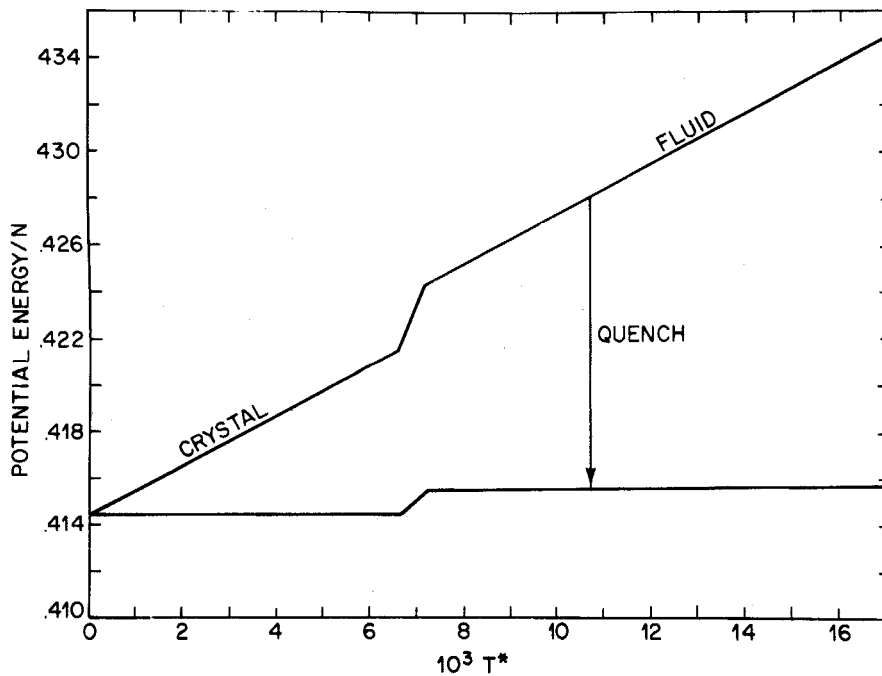


Figure 4. Potential energy mapping for the two-dimensional Gaussian core model at $\rho^* = 3^{-1/2}$. The upper curve gives the mean value $\langle\phi\rangle/N$ for the system at equilibrium. The lower curve gives the mean quench-state potential energies ϕ_0/N attained for quenches initiated at temperature T^* .

The most important conclusion to emerge from Fig. 4 is that the first-order melting transition is already inherent in the ϕ_0 function, that is, the mean quenched-state energies. ϕ_0/N begins to rise suddenly in the coexistence region above its essentially constant value below that region. It is hard to escape the conclusion that in the large-system limit ϕ_0/N would exhibit a mathematical singularity precisely at the onset of melting. To the extent that we can tell from our limited data it also appears that this limit function is singular at the upper temperature end of the melting range.

Another significant conclusion concerns the amount of potential energy removed by the quench, $(\langle\phi\rangle - \phi_0)/N$. In the low temperature crystal this quantity is close to linear in T^* owing to equipartition of thermal energy among harmonic phonon modes. But melting causes this quench energy to rise somewhat above the low temperature linear behavior. The only possible explanation is that the thermal excitation process is anharmonic for those regions $R(\alpha)$ which pertain to the fluid phase. In particular these regions, though quadratic near their minima, behave in a "softer-than-quadratic" fashion for higher degrees of thermal excitation.

IV. DISCUSSION

The computations reported in the preceding section amount only to a modest beginning. While the few quenches that have been carried out thus far serve to characterize ϕ_0/N qualitatively for the Gaussian core model in two dimensions, it is obvious that many more quenches need to be completed for a precise determination. Once this function is well in hand, integrations with respect to T^* from the high temperature ideal gas limit should permit at least some combination of G and F to be constructed.

Of course this would complete the numerical task only for the Gaussian interaction, whose repelling nature suffices to ensure the existence of a stable crystalline solid. It is also desirable in the two-dimensional regime to carry out the present quench method for interactions with attraction, such as the Lennard-Jones potential. Although quantitative changes would occur with this latter system, we do not expect any qualitative change in the nature of ϕ_0/N or of the quenched-state structures. In particular we expect that two-dimensional Lennard-Jones liquids will quench to polycrystalline mosaics that look similar to those already found with the Gaussian core model. Furthermore the melting transition points again should correlate with singularities in the large-system-limit ϕ_0/N .

The reason for initiating this work with a two dimensional application is simply that particle configurations can easily be visualized and described. The corresponding situation for three dimensional systems is more formidable, but the extension obviously must be undertaken in the near future. One anticipates that quenched liquids will yield polycrystalline mosaics, and that ϕ_0/N will continue to show mathematical singularities at the transition points.

It will be fascinating eventually to apply the technique in this paper to statistical mechanical models for real substances with polyatomic molecules. The normal alkanes [9] and water [10] are important cases for which moderately realistic potential energy functions now exist. Quenching their respective liquids will presumably produce molecular packings that have recognizably polycrystalline structures. But particularly for water where so many crystalline forms are known it is not obvious that all of the grains would have the structure of ordinary hexagonal ice. These computations are feasible, and it appears to us likely that they will be carried out during the next decade.

We are not aware of any modern work in liquid state theory that utilizes a thermally excited polycrystalline structure as its basis. It would seem that this is a fruitful direction for future effort, however.

In regards to the melting transition itself, combinatorial and energetic properties of stable particle packings need to be studied analytically in both two and three dimensions. The work reported in this paper suggest that progress in understanding these properties is a necessary prerequisite to a universal melting theory.

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