Hard-Sphere Glass and the Density-Functional Theory of Aperiodic Crystals

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A density-functional theory of freezing into an aperiodic lattice is presented. With use of free-energy functionals for inhomogeneous hard-sphere fluids, the stability of a density wave with the structure of Bernal random packing is evaluated. Although the properties of the transition are sensitive to the form of the direct correlation function, the present calculations indicate a limit of metastability at a density $\rho = 1.03$. The frozen lattice becomes more stable than the liquid at a density $\rho = 1.14$.

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The fascinating stability of glasses has attracted a great deal of theoretical attention recently.[1] At the same time, two rather different theories of melting of periodic crystalline solids have been very successful. The Kosterlitz-Thouless-Nelson-Halperin theory of melting[2-4] is based on a dislocation model of the liquid and has been particularly successful in two dimensions. The other approach, a mean-field theory based on the density-functional ideas from liquid-state physics, has been reinvigorated by Ramakrishnan and Yussouff[5] and others.[6-8] This theory is also quantitatively successful, especially in three dimensions, and has the advantage of making direct contact with the underlying intermolecular forces. Nelson[9] has beautifully shown how the disclination picture can be used to shed light on the three-dimensional glass problem. The theory suggests that there is an underlying phase transition to a Frank-Kasper–type phase with a complex unit cell.[10] In this paper we shall show how the density-functional theories can be used to describe a structurally stable but aperiodic phase or to describe crystalline phases with complex unit cells.

The picture of a glass as an aperiodic crystal is an old one to which many have subscribed. Ruelle has argued that there is no general theoretical argument that thermodynamically stable states must have periodic density distributions.[11] Indeed, the existence of Penrose's remarkable aperiodic tilings of the plane by two differently shaped tiles shows that such states may indeed be stable if the constituent particles are appropriately (and rather strangely) shaped.[12] Still, the question for the glass problem is whether such a packing for simple objects can be metastable. Starting with Bernal[13,14] many workers have constructed large regions of aperiodic structures that appear to be structurally sound. Evidence for the linear stability of such a packing to small few-particle displacements can be obtained from a self-consistent–phonon theory.[15]

In density-functional theories one seeks a minimum of the free energy which is considered to be a functional of the spatially varying, ensemble averaged, number density. The structure of the Euler-Lagrange equations for the density functionals used in the melting theory is very reminiscent of the mean-field equations for magnets with long-range interactions.[16] The mean-field equations for the anisotropic next-nearest-neighbor Ising (ANNI) model and similar models of structural phase transitions have been much investigated.[17] In one dimension these equations do have chaotic, i.e., aperiodic, solutions, but it has been shown that nearly periodic solutions with large unit cells are the truly metastable states.[18] The mathematics for more dimensions has not been fully developed, so the situation is less clear. Aubry has argued that there are such states and has commented upon the connection with glasses.[19]

The viewpoint we shall take in this paper is simpler (and a bit noncommittal on the mathematical issue). We shall assume that the large aperiodic structures that have been built can be continued to the thermodynamic limit. Making this assumption, we can use these structures as a skeleton upon which we can build a trial function for an aperiodic density distribution. With a single variational parameter, this trial function can accommodate both the uniform fluid state and an aperiodic state in which particles remain tethered to their sites in the amorphous lattice. This trial function can be used in variational expressions for the free energy, obtained from liquid-state theory, which contain the liquid-state direct correlation function as input. We show that at low density only the uniform state is stable but that at high density a metastable state with an aperiodic density distribution occurs. The transition to the aperiodic frozen state appears to be discontinuous. Because of the sensitivity of the results to the input liquid thermodynamic and structural data, we cannot pin down the transition point exactly, but it is near the values reported in computer simulation. Landau-Ginzburg treatments[20,21] have indicated that the transition should be weak. This does not seem to be confirmed by the present calculations but experience in the study of periodic-crystal freezing indicates that the present approximations can exaggerate the stability of the frozen state. We feel that our calculations do, however, give support to the basic notion that there is an underlying transition, from a liquid-state theory viewpoint.

The theory starts with the density functional used by Ramakrishnan and Yussouff. This functional consists of the ideal gas free-energy functional plus the interaction part of the free energy calculated to second order as an expansion about the uniform state:

$$F[\rho(\mathbf{x})]=F_{id}+F_{\text{int}}=\int d^3x\,\rho(x)[\ln\rho(x)-1]-\tfrac{1}{2}\int\int[\rho(x)-\rho_0]c(x,x';\rho_0)[\rho(x')-\rho_0]d^3x\,d^3x'+F_{\text{uni}}.$$

In this expression, $\rho(x)$ is the nonuniform single-particle density distribution, ρ_0 its mean value, and energy is measured in units of thermal energy, k_BT. The interaction part involves the direct correlation function of the fluid, $c(x,x';\rho_0)=c(|x-x'|,\rho_0)$ evaluated at the density ρ_0. F_{uni} is the excess free energy of the uniform liquid. For freezing,[5,6] and other problems such as the liquid interface,[22] more sophisticated free-energy functionals have been developed, but this simple form captures much of the essential physics. We use several approximations for the direct correlation function. The simplest is obtained from the exact solution of the Percus-Yevick (PY) integral equation for hard spheres.

We also use a more accurate $c(r)$ which has been obtained from a semiempirical approach due to Henderson and Grundke.[23] High-density values for $c(r)$ have not been addressed adequately in the literature, and those that have fall short, in terms of the densities of the glass with which we are concerned.[24,25] Faced with this ignorance of $c(r)$ expressions at high density, we have assumed a linear form for the tail of $c(r)$, which reduces to that of Henderson and Grundke for short-ranged correlations, and have adopted their $c(r)$ within the hard-sphere core.

Although theories of $c(r)$ at moderately high density (i.e., $\rho \leqslant 0.9$) have positive tails for short-ranged correlations,[24,25] Tarazona's successful analysis of the melting transition uses a negative tail in $c(r)$.[7] Clearly, there is uncertainty in $c(r)$ at high density *vis à vis* the density-functional theory. We feel that our *ad hoc* tail, in light of this uncertainty, has the virtues of variability and simplicity, enabling one to ascertain the sensitivity of the transition to correlation effects not incorporated in the PY theory. Consequently, we have proceeded with caution in our interpretation of transition data, and emphasize that our purpose in this Letter is simply to suggest a viable approach to the glass transition problem.

For our trial function we use a sum of Gaussians centered about the N lattice sites of a large amorphous lattice:

$$\rho(\mathbf{x})=\sum_{i=1}^{N}\rho_i(x;x_i)$$
$$=\left(\frac{\alpha}{\pi}\right)^{3/2}\sum_{i=1}^{N}\exp[-\alpha(x-x_i)^2].$$

The mean square displacement, α^{-1}, and the positions of the lattice sites, $\{X_i\}$, are adjustable parameters. Tarazona has used this sort of trial function for $\{x_i\}$ on a crystalline lattice, with, however, a different free-energy functional in his study of ordinary freezing.[8] Haymet's study of hard-sphere freezing uses a reciprocal-space description which is equivalent.[4] In these papers, the $\{x_i\}$ lie on a periodic lattice.

At present, we take the lattice sites to be given by the positions of particles in a random close packing obtained by the cluster growth algorithm of Bennett.[14] In principle, the lattice points might be relaxed from these positions in order to optimize the free energy. The nearest-neighbor distance, d_c, is adjusted so that the interior density of the cluster is equal to the uniform density of the system.

The ideal-gas part of the free energy is the most demanding to calculate because it is nonlinear and nonadditive. Given a complete realization of the $\{x_i\}$ it would be a straightforward but tedious numerical exercise to evaluate it, but we have developed instead two approximate formulas which give rather good bounds on the quantity. When α is large, the Gaussians do not overlap and F_{id} becomes simply $F_{id}(\alpha)=\frac{3}{2}\ln(\alpha/\pi)-\frac{5}{2}$. This is a lower bound, since $\rho(x)>\rho_i(x)$. The first corrections to this form can be expressed as a pairwise sum over the Bennett lattice, because the overlaps are weak. Similarly when α is small the density is nearly uniform and the entropy can be expressed as a pairwise sum over the lattice which is an upper bound. Numerical calculations show that these formulas mesh rather well.

In fact the free-energy minima occur at such large α that the limiting large-α formula suffices. $F_{\text{int}}(\alpha)$ can again best be calculated in terms of the pair distribution function of the reference lattice:

$$F_{\text{int}}(\alpha)$$
$$=N[C(0)+V_1(\alpha)+\rho\int V_2(\alpha,x)g^{(0)}(x)d^3x].$$

In this expression, $V_1(\alpha)$ is the self-interaction of a single Gaussian:

$$V_1(\alpha)=\int\rho_0(x;0)\rho_0(x';0)c(x,x')d^3x\,d^3x';$$

V_2 is an averaged interaction between two distinct Gaussians:

$$V_2(\alpha;x_1)=\int\rho_0(x;0)c(x,x')\rho_1(x';x_1)d^3x\,d^3x';$$

and $C(0)$ is the zero-wave-vector direct correlation function.

For the PY $c(r)$, the entropic term more than balances the interaction term, so that no minimum at finite α results at the densities considered. However, the sum of the ideal-gas terms with the interaction term for the more accurate $c(r)$ is plotted at several densities in Fig. 1(a). There is always a local minimum at $\alpha = 0$. At a density of $\rho_0 = 1.03$, the localized minimum appears at $\alpha = 287$. This minimum is due to competition of the entropic and interaction term. For every density at which we obtain a free-energy minimum, we determine the minimum free-energy values as a function of density. The total free energy per particle, relative to the uniform fluid, for the Henderson-Grundke $c(r)$, is plotted versus density in Fig. 1(b). The free energies cross at a density $\rho_T = 1.14$. Although this curve suggests a first-order phase transition it proved to be impossible to carry out a Maxwell construction because most approximate free energies for the liquid gave negative pressures when combined with our relative free-energy results. Tarazona has indicated in his study of the freezing into the fcc crystal that the truncation of the free-energy expansion in ρ to second order exaggerates the stability of the crystalline phase. This is likely the cause of the negative pressures. In addition, calculations indicate the sensitivity of solid stability to the tail of $c(r)$. Because of the *ad hoc* nature of this tail, our negative pressures are presumably rectifiable with the use of more accurate $c(r)$ expressions in the future. Parenthetically, the Maxwell construction (i.e., double tangent) which we used to locate the coexistence densities for the liquid and solid is identically equivalent to the equality of grand potentials used in the original formulation of density-functional theory by Ramakrishnan and Yussouff.[26]

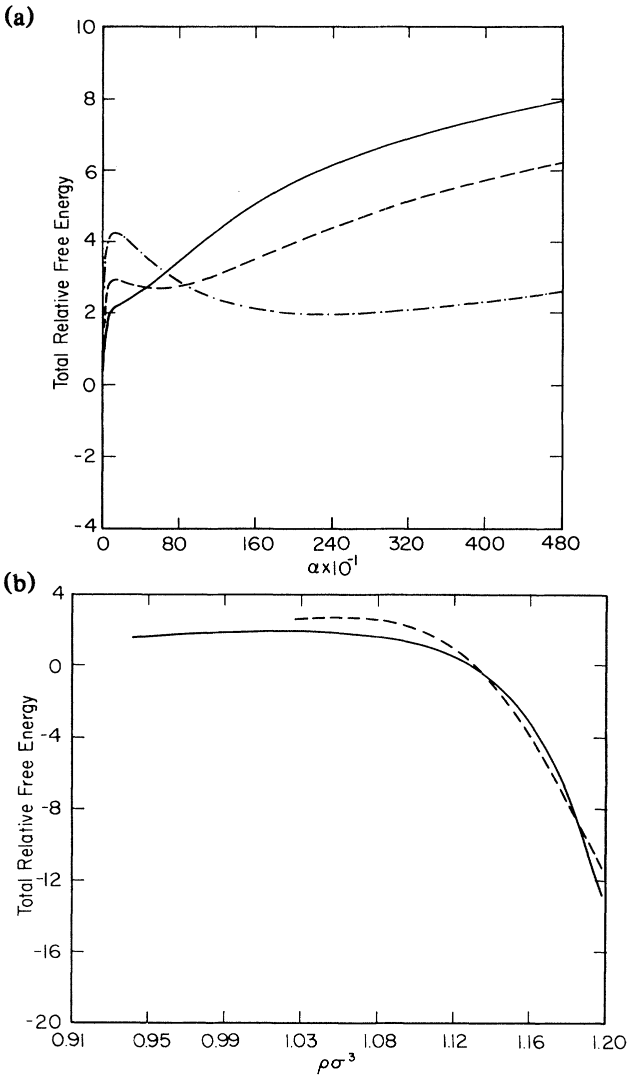

FIG. 1. Total free energy per particle, relative to uniform fluid. (a) Versus α. The Bennett structure is assumed. Solid curve, $\rho\sigma^3 = 1$; dashed curve, $\rho\sigma^3 = 1.05$; dot-dashed curve, $\rho\sigma^3 = 1.1$. (b) Versus $\rho\sigma^3$, with approximate Henderson-Grundke $c(r)$. Solid curve, curved-space structure; dashed curve, Bennett structure.

It is important for our theory that the set of fiducial points $\{x_i\}$ be realizable in ordinary three-dimensional space. Nevertheless it is amusing to compare the results with those for the hypothetical icosahedral crystal which exists in curved space. The pair distribution is given by Sadoc as a sum of delta functions.[27] The minimum density for the aperiodic state is $\rho = 0.95$ at which the α value is 98.5. The density at which the crystalline free energy crosses the liquid is $\rho = 1.135$. This is also shown in Fig. 1(b). Thus the hypothetical curved-space packing is somewhat more stable than the Bennett packing. Clearly annealing effects and other nonequilibrium phenomena will play a role in determining the exact transition point, but the agreement is heartening.

The present theory describes a kind of liquid-glass thermodynamic transition, starting by an expansion about the liquid state. As such it is most appropriate near the transition. The crossing density ρ_T is close to the devitrification densities observed in simulation. The calculations presented here give evidence that a transition to an aperiodic crystal is reasonable from the point of view of approximate liquid-structure theory. The transition appears to be discontinuous but critical fluctuation effects like those described by defect theories will play a significant role in determining the nature of the transition and coexistence parameters. In addition, because a particular amorphous lattice is assumed, the present theory does not rule out the possibility that some structure that is periodic but with a large unit cell is a better description. For these reasons our results must be viewed as suggestive. We feel that these initial results, showing the possibility of a thermodynamic transition, will encourage further work along these lines. We should bear in mind, however, that the analogous situation arose in the theory of the spin-glass, where the original mean-field treatments indicated thermodynamic phase transitions, while subsequent theories, incorporating relaxation phenomena, resulted in smoothed-out transitions. These nonequilibrium phenomena may be responsible for a number of interesting glassy behaviors, as Parisi suggests.[28] Although the nature of the transition was changed from the original results of mean-field theory, these initial approaches proved illuminating. In addition because the mean-field theory makes contact with the underlying forces, through the integral equation theories of liquid structure, the present approach should be valuable in understanding the molecular basis of the glass transition. In view of the sophisticated state of liquid-structure calculations, one can hope to extend these ideas to more complex systems, such as soft-sphere glasses, binary-mixture glasses, and glasses made up of polyatomic molecules.

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[1] See, for example, articles in *Topological Disorder in Condensed Matter,* edited by T. Ninonaya and F. Yonezawa (Springer, Berlin, 1983).

[2] J. M. Kosterlitz and D. J. Thouless, J. Phys. C **6**, 1181 (1973).

[3] B. Halperin and D. Nelson, Phys. Rev. Lett. **41**, 121 (1978).

[4] D. Nelson and B. Halperin, Phys. Rev. B **19**, 2457 (1979).

[5] T. V. Ramakrishnan and M. Yussouff, Phys. Rev. B **19**, 2775 (1979); M. Yussouff, Phys. Rev. B **23**, 5871 (1983).

[6] A. D. J. Haymet and D. W. Oxtoby, J. Chem. Phys. **74**, 2559 (1981), and **76**, 6262 (1982).

[7] A. D. J. Haymet, J. Chem. Phys. **78**, 4641 (1983).

[8] P. Tarazona, Mol. Phys. **52**, 871 (1984).

[9] D. R. Nelson, Phys. Rev. Lett. **50**, 982 (1983), and Phys. Rev. B **28**, 5515 (1983).

[10] F. C. Frank and J. S. Kasper, Acta. Crystallogr. **11**, 184 (1958), and **12**, 483 (1959).

[11] D. Ruelle, Physica (Utrecht) **113A**, 619 (1982).

[12] M. Gardner, Sci. Am. **236**, 110 (1977).

[13] J. D. Bernal, Proc. Roy. Soc. London, Ser. A **280**, 299 (1964).

[14] C. H. Bennett, J. Appl. Phys. **43**, 2727 (1972).

[15] J. P. Stoessel and P. G. Wolynes, J. Chem. Phys. **80**, 4502 (1984), and unpublished calculations.

[16] P. Bak, Rep. Prog. Phys. **45**, 587 (1982).

[17] M. Fisher and W. Selke, Phys. Rev. Lett. **44**, 1502 (1980).

[18] E. Fradkin, O. Hernandez, B. A. Huberman, and R. Pandit, Nucl. Phys. **B215**, 137 (1983).

[19] S. Aubry, J. Phys. (Paris) **44**, 147 (1983).

[20] S. Alexander and J. McTague, Phys. Rev. Lett. **41**, 702 (1978).

[21] M. Widom and D. R. Nelson, to be published.

[22] Y. Singh and F. F. Abraham, J. Chem. Phys. **67**, 537 (1977).

[23] Douglas Henderson and E. W. Grundke, J. Chem. Phys. **63**, 601 (1975).

[24] F. J. Rogers and D. A. Young, Phys. Rev. A **30**, 999 (1984).

[25] B. B. Deo and A. C. Naik, Phys. Rev. A **28**, 1700 (1983).

[26] See, for example, Radu Balescu, in *Equilibrium and Nonequilibrium Statistical Mechanics* (Wiley, New York, 1975).

[27] J. F. Sadoc, J. Non-Cryst. Solids **44**, 1 (1981).

[28] M. Mezard *et al.*, J. Phys. (Paris) **45**, 843 (1984).