

Orientational Order in Liquids: A Possible Scenario of Freezing

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A new model of liquid-solid freezing, based on the orientational order in a three-dimensional liquid, is proposed. The novel aspect of the model is the inclusion of the coupling between the orientational and elastic degrees of freedom in a dense liquid. This allows for the explicit computation of several thermodynamic quantities of interest near the freezing transition.

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One of the most challenging problems in contemporary statistical physics is the freezing transition in a three-dimensional classical liquid. Despite the accumulation of considerable experimental and computer simulation data¹⁻³ the theoretical description of freezing remains unsatisfactory. Almost all equilibrium statistical-mechanical theories of freezing at the molecular level are *de facto* extensions of the original ideas of Kirkwood and Monroe⁴ and are in disagreement with experimental and computer-simulation data.⁵ In this Letter we outline a novel approach to the theory of freezing. We state only the main results obtained within a simplified version of our approach which bears a certain similarity with the *compressible* three-state Potts model. Details of the calculations and possible extensions to deal with dynamics will be reported elsewhere.

It has been recently argued that the remarkable properties of dense supercooled liquids and glasses are *dynamical* in origin.⁶⁻⁸ They result from the extreme sluggishness of single-particle motions—reflected among other things in the change of the particle diffusion mode from Fickian to hoppinglike. Accompanying this is a dramatic increase of the shear viscosity. In fact, supercooled liquids and glasses exhibit properties not much different from those of isotropic elastic media. In a sense a dense cooled liquid “looks liquid” only when probed at sufficiently low frequencies. The dynamical models of dense liquids, supercooled liquids, and glasses rely on the concept of a local “cage” felt by a single particle. A picture like this had been invoked in the early days of neutron scattering from liquids wherein the experimental data had been interpreted on the basis of a local quasicrystalline model of liquids.⁹ A similar concept seems to be in agreement with computer-simulation data also.¹⁰ At the equilibrium level the cage effect manifests itself in the existence of *local orientational order* in liquids which is not only long lived but is spatially long ranged as well, at temperatures not far above T_f . The idea of the local orientational order in liquids is not new. It is implicit in the Frenkel model¹¹ of the liquid state and

has been employed recently in various guises by Hess,¹² Mitus and Patashinskii,¹³ and Haymet.¹⁴

The local orientational order cannot be easily described by the conventional liquid-state theory, i.e., the one involving one- and two-particle distribution functions. The difficulty is that the local order has just a minor influence on the pair-correlation function and, hence, on the static structure factor. Experimentally, the pair-correlation function shows only smooth changes, e.g., a splitting of the second peak and no dramatic divergences near T_f as predicted, for instance, in the theory of Schneider *et al.*¹⁵ In fact, the information about the local orientational order and the incipient lattice structure are embodied in higher-order distribution functions; one needs at least four-particle distribution functions to describe cubic symmetries. Structures other than cubic require even higher-order correlation functions. The fact that four-particle functions do not simply factor into two-particle functions, as assumed in the Kirkwood-type theories, is already suggested in the computer studies of the three-particle correlation function. In general, therefore, one needs to build a molecular theory on the four-particle distribution function ρ_4 and that can be done if we assume the free energy F to be a *functional* of ρ_4 . For dense cold liquids in which the local cage concept is applicable, $\rho_4(\mathbf{r}_1, \dots, \mathbf{r}_4)$ can actually be related to the probability of having, at an arbitrary point \mathbf{r} , a local triad of vectors \mathbf{h}_i ($i=1, 2, 3$). These vectors define the local coordinates in a liquid according to the orientational order; one can construct them, for example, with the aid of local Wigner-Seitz cells. Thus, the main object of the theory is the probability density $\rho(\mathbf{r}, \{\mathbf{h}\})$. This description is reminiscent of that of a crystal, with continuously distributed dislocations, by means of anholonomic local frames.^{16,17} At this stage our approach has to rely on assumptions common to all other local-order theories of liquids, viz. that the free energy F can be written as a quadratic functional of ρ . Thus, expanding $\rho(\mathbf{r}, \{\mathbf{h}\})$ into properly chosen spherical harmonics (irreducible tensors of rank four^{12,13} or the Wigner rotation matrices¹⁴) one obtains

$$F\{\Lambda\} = \frac{1}{2} V^{-2} \int d^3 R_1 d^3 R_2 E_{AB}(\mathbf{R}_1, \mathbf{R}_2) \Lambda^A(\mathbf{R}_1) \Lambda^B(\mathbf{R}_2), \quad (1)$$

where $\Lambda^A(\mathbf{R}_i)$ stands for properly chosen variables describing the local order at the point \mathbf{R}_i , and V is the volume

of the system. Here and elsewhere the summation convention is used.

From this point onward, however, our analysis departs from the existing ones. We assume now not only that the fields Λ^A describe the instantaneous orientational order but that they are also coupled to the remaining degrees of freedom of the liquid. When the latter evolve, the adjacent cages move slightly apart but they preserve their identity, in view of the assumed time-scale separation. Therefore, the coupling between the neighboring Λ becomes a function

$$F = \frac{1}{2} V^{-2} \int d^3 R_1 d^3 R_2 E_{AB}^0(\mathbf{R}_1 - \mathbf{R}_2) \Lambda^A(\mathbf{R}_1) \Lambda^B(\mathbf{R}_2) + V^{-2} \int d^3 R_1 d^3 R_2 G_{AB}^{\alpha\beta}(\mathbf{R}_1 - \mathbf{R}_2) \nabla_\alpha u_\beta(\mathbf{R}_1) \Lambda^A(\mathbf{R}_1) \Lambda^B(\mathbf{R}_2) + F_0\{\mathbf{u}\}. \quad (2)$$

The coupling between the orientational order and elastic degrees of freedom is therefore linear in the distortion tensor $\nabla_\alpha u_\beta = \epsilon_{\alpha\beta} + \omega_{\alpha\beta}$, $\epsilon_{\alpha\beta}$ being the elastic strain tensor and $\omega_{\alpha\beta} = (\nabla_\alpha u_\beta - \nabla_\beta u_\alpha)/2$ the elastic rotation tensor. The latter is related, in lattice elasticity, to the density of dislocations. The role of the ω - Λ coupling becomes important in the theory of melting. It should be noted that Eq. (2) describes the most general coupling between the distortion and the internal stresses due to orientational order allowed in linear elasticity. Since it is that coupling and not the mode-mode-like one between the elastic deformation modes which is pertinent near freezing, neglecting ω we can write F_0 as in conventional elasticity theory:

$$F_0 = F_{el} = \frac{1}{2} \bar{C}_{\alpha\beta\alpha'\beta'} V^{-1} \int d^3 R_1 \epsilon^{\alpha\beta}(\mathbf{R}_1) \epsilon^{\alpha'\beta'}(\mathbf{R}_1). \quad (3)$$

Here $\bar{C}_{\alpha\beta\alpha'\beta'}$ stands for the "bare" elastic coefficients of the system, the measurable ones being renormalized by the coupling between the fields Λ and ϵ . The Hamiltonian having been specified by (2) and (3) the thermodynamic properties of the system can be evaluated from the partition function

$$Z = \int D\Lambda D\epsilon \exp(-\beta F), \quad (4)$$

where the integration is carried out over the entire functional space of orientational and elastic degrees of freedom, and $\beta = (k_B T)^{-1}$.

A complete analysis of the functional integral in (4) is beyond reach and one has to resort to approximations, the simplest being the mean-field theory. Within the mean-field approach the "rigid" part of the Hamiltonian [given by the first term on the right of

of $\mathbf{R}_i - \mathbf{R}_j = (\mathbf{R}_i^0 - \mathbf{R}_j^0) + \mathbf{u}_i(\mathbf{R}_i^0) - \mathbf{u}_j(\mathbf{R}_j^0)$, where \mathbf{u}_i describes the instantaneous displacement of the cage from its averaged position. A complete description of the liquid may then be given by adding to (1) the free energy of the remaining degrees of freedom $F_0\{\mathbf{u}\}$ which we describe by means of the displacement field \mathbf{u} . The coupling between the orientational and translational degrees of freedom in a similar context was discussed in Ref. 18 but in a very different way. Now, expanding E_{AB} around the averaged cage positions R_i^0 , we obtain a field theoretic model with the Hamiltonian $F = F\{\Lambda, \mathbf{u}\}$ given as

(2)] is known to lead to a first-order phase transition with the averaged value $\langle \Lambda \rangle$ undergoing a jump at T_f , interpreted here as the freezing temperature. The inclusion of elastic degrees of freedom is expected to enhance the first-order transition as in compressible Ising models.¹⁹

The connection between freezing and the occurrence of finite orientational order can be interpreted in the following way. The local cage concept in dense liquids makes sense when the adjacent cages are on the average separated by a distance R_{ij}^0 which is already compatible with the lattice constant of the incipient crystal. This fact is reflected in the moderate increase in the value of the first maximum in the radial correlation function near freezing. Thus it is the local misfit of Λ which distinguishes a liquid and a solid on either side of T_f . The jumps in $\langle \Lambda \rangle$ and the Λ - Λ correlation at T_f result in changes at T_f of several important macroscopic quantities. They are (i) the volume, (ii) the specific heat, and (iii) the elastic compliance.²⁰ We outline below the results for the quantities (i), (ii), and (iii).

The linear coupling between $\epsilon_{\alpha\beta}$ and $\Lambda^A \Lambda^B$ allows us to carry out the integral over the elastic degrees of freedom exactly. As a result the mean value of the deformation $\langle \epsilon_{\alpha\beta} \rangle$ turns out to be

$$\langle \epsilon_{\alpha\beta}(\mathbf{R}_1) \rangle = V^{-1} \int d^3 R_2 \bar{S}_{\alpha\beta\gamma\delta} G_{AB}^{\gamma\delta} \langle \Lambda^A(\mathbf{R}_1) \Lambda^B(\mathbf{R}_2) \rangle, \quad (5)$$

where \bar{S} is the elastic compliance tensor (inverse of \bar{C}). From (5) we may write a general expression for the volume change at freezing as

$$\Delta V/V = V^{-1} \text{Tr} \int d^3 R_1 (\langle \epsilon_{\alpha\beta}(\mathbf{R}_1) \rangle_+ - \langle \epsilon_{\alpha\beta}(\mathbf{R}_1) \rangle_-) = V^{-2} \text{Tr} \int d^3 R_1 d^3 R_2 \bar{S}_{\alpha\beta\gamma\delta} G_{AB}^{\gamma\delta} [\langle \Lambda^A(\mathbf{R}_1) \Lambda^B(\mathbf{R}_2) \rangle_+ - \langle \Lambda^A(\mathbf{R}_1) \Lambda^B(\mathbf{R}_2) \rangle_-], \quad (6)$$

where $\langle \dots \rangle_\pm$ denote the values of the bracketed quantities above and below the transition, respectively. Similar

general formulas can be written down for the specific heat and the elastic compliance.

The explicit evaluation of quantities as in (6) requires specification of the rigid part of the Hamiltonian for the Λ variables. We choose, for the sake of simplicity and for the purpose of this presentation, a model analogous to the three-state Potts model. This assumption allows us to carry out all the calculations explicitly and does not miss, we believe, any essential feature of the problem. Indeed, the shape of the free energy for the three-state Potts model, within the mean-field approximation,²⁰ is qualitatively the same as that calculated numerically for the continuous model by Haymet,¹⁴ or for the four-state model by Mitus and Patashinski.¹³

The local orientation of the cage, in our model, is then represented by a triad constituted of three vectors \mathbf{h}_i rigidly "welded" together at a mutual angle $\pi/2$. In addition, the triad is viewed to have only *three* discrete orientations, obtainable from one another by the interchange of any two of the three vectors \mathbf{h}_i . Each of these orientations has an occupational probability $\langle \Lambda^A \rangle$ where Λ^A ($A=1,2,3$) can be represented by a 3×3 matrix with the "projection" property $\Lambda^A \Lambda^B = \Lambda^A \delta^{AB}$ (no sum on A). Since we have assumed cubic symmetry here, the coupling constants E_{AB}^0 depend only on the relative orientation of the triads, leaving us with just two independent constants E^\perp and E^\parallel corresponding to whether the triads are mutually perpendicular or parallel.

In the liquid (disordered) phase $\langle \Lambda^A \rangle = n^A$ simply equals $\frac{1}{3}$. On the other hand, the ordered phase is most conveniently characterized by an order parameter z_0 related to n^A via $z_0 = 1 - 3n^\parallel = \frac{1}{2}(3n^\perp - 1)$, where \parallel and \perp denote directions in the triad space.²⁰ Setting $f_A = E_{AB} n^B$ and $g_{AB} = G_{AC}^{\alpha\beta} \bar{S}_{\alpha\beta\gamma\delta} G_{BD}^{\gamma\delta} n^B n^D$, we write the

transcendental equation for n^A as

$$n^A = \exp\beta(f_A + g_{AA}) \left[\sum_{c=1}^3 \exp\beta(f_C + g_{CC}) \right]^{-1}. \quad (7)$$

The analysis of this equation is standard leading to the solution $n^A = \frac{1}{3} \forall A$ for $T > T_f$ and predicting a jump at T_f in the value of z_0 ($z_0 = 0$ for $T > T_f$). At each T below T_f we can solve for z_0 from (7) and that allows us to derive a closed-form expression for the volume change. Within the mean-field approach the correlation function $\langle \Lambda^A \Lambda^B \rangle$ in the integrand of (6) can be replaced by $(n^A - \frac{1}{3})(n^B - \frac{1}{3})$, and hence

$$\begin{aligned} \frac{\Delta V}{V} &= \bar{S}_{\alpha\beta\gamma\delta} G_{AB}^{\gamma\delta} (n^A - \frac{1}{3})(n^B - \frac{1}{3}) \\ &= \frac{2}{3} z_0^2 \bar{S}_{\alpha\beta\gamma\delta} \Delta G^{\gamma\delta} = z_0^2 K, \end{aligned} \quad (8)$$

where $\Delta G^{\gamma\delta}$ is the difference in the values of the coupling constant G [see (2)] for parallel and perpendicular arrangements of triads.

Note the correct dependence of ΔV in (8) on the square of the order parameter z_0 and on the bare longitudinal compliance \bar{S} , i.e., on the bare bulk modulus of the liquid.²² Since the restriction to the three-level model has been imposed more as a mathematical simplicity than a physical necessity we expect the formula (8) to hold generally, with, of course, different values of the coefficient K .

Next, we calculate the change in the specific heat at the freezing transition:

$$\Delta C = (\Delta C)_{\text{smooth}} - K_1 z_0 dz_0/dT, \quad (9)$$

where K_1 depends on ΔE , ΔG , and E .

Finally, we turn to the question of the *effective* elastic coefficients. The quantity of interest is the elastic compliance tensor S which measures the response to a small stress and is given by

$$S^{\alpha\beta\gamma\delta} = V^{-2} \int d^3 R_1 d^3 R_2 \{ \langle \epsilon^{\alpha\beta}(\mathbf{R}_1) \epsilon^{\gamma\delta}(\mathbf{R}_2) \rangle - \langle \epsilon^{\alpha\beta}(\mathbf{R}_1) \rangle \langle \epsilon^{\gamma\delta}(\mathbf{R}_2) \rangle \}. \quad (10)$$

The mean-field analysis enables us to express the strain correlation in terms of the Λ - Λ correlation $C(\mathbf{R}_1 - \mathbf{R}_2)$ itself, which, upon integration over \mathbf{R}_1 and \mathbf{R}_2 , yields the zero-"wave-vector" Fourier component $\bar{C}(\mathbf{q}=0)$. Thus, we find that the change of the elastic compliance due to the finite orientational order reads

$$\Delta S^{\alpha\beta\gamma\delta} = K^{\alpha\beta\gamma\delta} z_0^2 \bar{C}(\mathbf{q}=0), \quad (11)$$

where $K^{\alpha\beta\gamma\delta}$ depends on the bare compliance \bar{S} and the coupling constant G . We may now evaluate $\bar{C}(q)$ within the Ornstein-Zernike-type approximation, leading to (for $T > T_f$)

$$\Delta S^{\alpha\beta\gamma\delta} \sim K^{\alpha\beta\gamma\delta} z_0^2 (1 - \alpha T/T_f)^{-1}, \quad (12)$$

where α is a numerical factor ($\alpha < 1$). In the three-state Potts model²¹ α turns out to be 0.92. The formu-

la (12) is particularly interesting; it shows how the presence of long-range orientational order enhances the longitudinal and shear moduli of the system as the freezing point is approached. A similar phenomenon has been observed in $d=2$ computer simulations^{23,24} with a scenario of orientational order somewhat different from ours ($d=3$).

We conclude, therefore, that our model allows for a systematic calculation of various thermodynamic quantities at freezing.²² Our interpretation of the coupling between the elastic and orientational degrees of freedom appears distinct from that of Ref. 13 and Ref. 18; it enables us to make a direct contact with the phenomenological treatment of Ref. 12. We stress once more that the three-state approximation we have used is, in fact, inessential. Similar results can be ob-

tained for higher-state models without gaining any additional physical insight.

There are several possible extensions of our model, barring the ones mentioned above. The most important of these is the analysis of dynamics of orientational order. Following ideas outlined in Ref. 20 we can introduce "orientational flips" in much the same manner as "spin flips" in the Glauber version of the kinetic Ising model. This has to be done, of course, together with the dynamics of elastic degrees of freedom. The completion of that program would lead automatically to the calculation of the dynamic structure factor $S(\mathbf{q}, \omega)$ for long wavelength and low frequencies. At the freezing transition, $S(\mathbf{q}, \omega)$ reveals a narrow peak which exhibits "critical slowing down," i.e., the power-law character of the peak width. Similar behavior of the central peak at freezing is expected in view of the molecular-level⁶⁻⁸ and purely hydrodynamical²⁵ arguments. Work along this line is in progress.

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