

Freezing of a Quantum Hard-Sphere Liquid at Zero Temperature: A Density-Functional Approach

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Quantum freezing of the Bose hard-sphere liquid is described by an extension of the classical modified weighted-density approximation to nonuniform *quantum* liquids at zero temperature. The theory requires structural and thermodynamic information for the corresponding *uniform* quantum liquid, which we have chosen to take, for the purpose of illustration, from the paired phonon analysis. Predictions for solid-phase energies and for freezing parameters are in generally good agreement with available simulation data.

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A fundamental application of the density-functional method¹ is to the freezing transition in simple liquids. Using information on the structure and thermodynamics of the *uniform* liquid, the method leads to predictions for the densities of the coexisting liquid and solid phases, the latent heat of transition, and the Lindemann parameter. Although agreement with simulation results tends to vary with the system studied and with the version of the method used, especially notable success has been obtained in the important case of the *classical* hard-sphere liquid, where the predicted freezing parameters agree with simulation usually to within a few percent.¹ An interesting issue, therefore, is the manner in which the general method may be extended from classical to *quantum* systems, and whether, in particular, it can illuminate the physical nature of the freezing transition in quantum liquids. Recently, one version of the density-functional method, the Ramakrishnan-Yussouff theory,² has been extended³⁻⁵ and applied to freezing of a Lennard-Jones model of ⁴He at finite temperatures,³ and also to freezing (Wigner crystallization) of the ground-state Fermi one-component plasma.⁴ The purpose of this Letter is first to report a general extension of a quite *different* version of the method, the modified weighted-density approximation,^{6,7} from classical systems to quantum systems at zero temperature, and then to demonstrate its utility in the specific case of freezing of a Bose liquid of *hard spheres*.

In a density-functional approach to nonuniform quantum liquids at zero temperature the central quantity is the total ground-state energy $E[\rho]$, a *unique* functional⁸ of the one-particle density $\rho(\mathbf{r})$. In the absence of an external potential, the functional can be conveniently separated by writing

$$E[\rho] = E_{\text{id}}[\rho] + E_c[\rho], \quad (1)$$

where $E_{\text{id}}[\rho]$ is the *ideal-gas* energy, the energy of the nonuniform system without interactions, and $E_c[\rho]$ is the *correlation* energy, due to interatomic interactions and exchange. The advantage of this separation is that $E_{\text{id}}[\rho]$ can be treated exactly. In contrast, $E_c[\rho]$ is un-

known for nonuniform systems, and is here approximated by a simple extension to nonuniform ground-state quantum liquids of the modified weighted-density approximation⁶ (MWDA). The basis of the MWDA is the assumption that the average correlation energy per particle of the *nonuniform* system can be equated to its counterpart for the *uniform* liquid evaluated at a *weighted* density assumed to depend on a weighted average over the volume of the system of the (spatially varying) physical density, i.e.,

$$E_c^{\text{MWDA}}[\rho]/N \equiv \epsilon(\hat{\rho}), \quad (2)$$

where N is the number of particles, ϵ is the uniform-liquid correlation energy per particle, and $\hat{\rho}$ is *defined* by

$$\hat{\rho} \equiv \frac{1}{N} \int d\mathbf{r} \rho(\mathbf{r}) \int d\mathbf{r}' \rho(\mathbf{r}') w(\mathbf{r} - \mathbf{r}'; \hat{\rho}). \quad (3)$$

As in the classical formulation,^{6,7} the *self-consistent* choice of the density argument of the "weight function" w in Eq. (3) is essential. To ensure that the approximation is exact in the limit of a uniform liquid [$\rho(\mathbf{r}) \rightarrow \rho$], w must be normalized, i.e.,

$$\int d\mathbf{r}' w(\mathbf{r} - \mathbf{r}'; \rho) = 1. \quad (4)$$

A *unique* determination of w follows from requiring that $E_c^{\text{MWDA}}[\rho]$ satisfies

$$\lim_{\rho(\mathbf{r}) \rightarrow \rho} \left(\frac{\delta^2 E_c^{\text{MWDA}}[\rho]}{\delta \rho(\mathbf{r}) \delta \rho(\mathbf{r}')} \right) = v(|\mathbf{r} - \mathbf{r}'|; \rho), \quad (5)$$

where $v(|\mathbf{r} - \mathbf{r}'|; \rho)$ is to be interpreted as an extension to quantum liquids of the classical Ornstein-Zernike direct correlation function. Equation (5) ensures that a functional Taylor-series expansion of $E_c^{\text{MWDA}}[\rho]$ about the density of a uniform reference liquid is exact to second order, *and* includes approximate terms to all higher orders.^{6,7}

From Eqs. (2)–(5), it is now straightforward to show that the weight function is given (in Fourier space) by

the simple relation

$$w(k; \rho) = \frac{1}{2\epsilon'(\rho)} [v(k; \rho) - \delta_{k,0} \rho \epsilon''(\rho)], \quad (6)$$

where primes on ϵ denote derivatives with respect to density. We note from Eqs. (4) and (6) that

$$v(k=0; \rho) = 2\epsilon'(\rho) + \rho \epsilon''(\rho), \quad (7)$$

which may be interpreted as a "quantum compressibility rule."

Equations (2), (3), and (6) now constitute the MWDA for a nonuniform *quantum* liquid at zero temperature. For the Bose hard-sphere system, we have chosen to compute the required liquid-state information, ϵ and $v(k)$, *via* the paired phonon analysis⁹ (PPA). The PPA gives approximations both for ϵ and for the structure factor $S(k)$, from which we then obtain $v(k)$ from the simple relation¹⁰

$$v(k) = \frac{\hbar^2 k^2}{4m} \left[\frac{1}{S^2(k)} - 1 \right], \quad (8)$$

where m is the mass of a particle. It is important to mention, however, that the PPA does not guarantee consistency between ϵ and $v(k)$, in the sense that the compressibility rule [Eq. (7)] is not satisfied exactly. Therefore, in order to ensure that Eq. (7) is satisfied, we have *scaled* the PPA $v(k)$ by the factor $(2\epsilon' + \rho\epsilon'')/v(k=0)$, resulting in an increase in magnitude of about 20% (see below).

The main steps in the application to freezing are (i) parametrization of the solid density, (ii) minimization of the total solid energy with respect to the parametrized density, and (iii) location of the liquid-solid transition. The parametrization of the solid density $\rho_s(\mathbf{r})$ requires first, the *choice* of a crystal structure and second, an assumption for the form of the density distribution. As in previous studies of the *classical* hard-sphere system, we have assumed a perfect crystal with a simple Gaussian form,

$$\rho_s(\mathbf{r}) \equiv \left(\frac{\alpha}{\pi} \right)^{3/2} \sum_{\mathbf{R}} e^{-\alpha |\mathbf{r}-\mathbf{R}|^2}, \quad (9)$$

where α is a "localization parameter" determining the width of the Gaussians centered on the lattice sites at positions \mathbf{R} . This assumption is suggested by the Green's-function Monte Carlo simulation of a Lennard-Jones model of ^4He by Whitlock *et al.*,¹¹ who examined the solid density and concluded it to be spherically symmetric about a given lattice site with only small positive deviations from Gaussian behavior in the tail of the distribution. To our knowledge no such test has been performed for Bose hard spheres. Nevertheless, since we expect the hard-sphere and Lennard-Jones solids to exhibit rather similar behavior, we judge these simulation results, and the ensuing predictions of the MWDA, to be reasonable justification for our use here of Eq. (9).

From Eqs. (6) and (9), Eq. (3) now takes the form

$$\hat{\rho}(\alpha, \rho_s) = \rho_s \left[1 + \frac{1}{2\epsilon'(\hat{\rho})} \sum_{\mathbf{G} \neq 0} e^{-G^2/2\alpha} v(\mathbf{G}; \hat{\rho}) \right], \quad (10)$$

where ρ_s is the average solid density, and G the magnitude of the reciprocal-lattice vector \mathbf{G} of the solid density. This implicit relation for $\hat{\rho}$ can be easily solved (for fixed α and ρ_s) by numerical iteration,¹² and the approximate correlation energy E_c^{MWDA} is then given by Eq. (2). In the case of *nonoverlapping* Gaussians—a good approximation at densities near freezing—the ideal-gas energy E_{id} takes the particularly simple form $E_{\text{id}}/N \approx 3\hbar^2\alpha/4m$, identical to the form usually assumed in variational Monte Carlo simulations,¹³ leading finally to

$$\frac{E^{\text{MWDA}}(\alpha, \rho_s)}{N} \approx \frac{3}{4} \frac{\hbar^2}{m} \alpha + \epsilon(\hat{\rho}(\alpha, \rho_s)), \quad (11)$$

which is to be minimized with respect to α at *fixed* ρ_s . Figure 1 illustrates the minimization procedure, showing separately the dependence of the ideal-gas and correlation energies on α . For simplicity, we have plotted for E_{id} only the linear approximation, though this is strictly valid only for $\alpha\sigma^2 > 5$. Note that E_{id} increases with α , strongly *opposing* localization of the atoms about lattice sites, while E_c falls off rapidly with α , strongly *favoring* localization. The competition between E_{id} and E_c may result—for sufficiently high ρ_s (as in Fig. 1)—in a minimum in the *total* energy at nonzero α , implying a mechanically stable solid. *Thermodynamic* stability of the solid relative to the liquid is determined by comparing the liquid and solid energies. By varying ρ_s and repeating the minimization procedure, the solid-phase en-

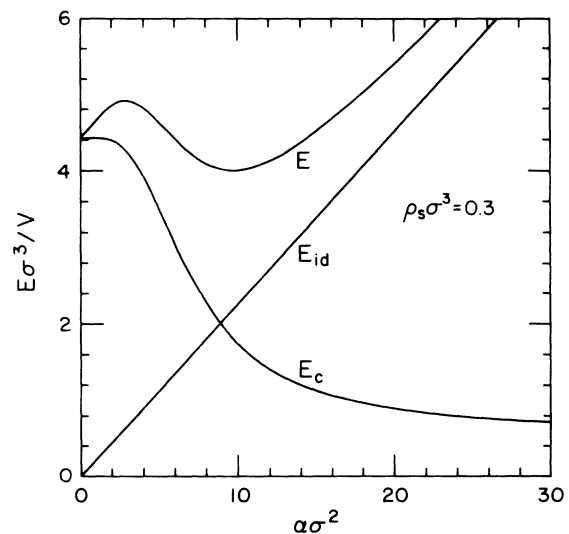


FIG. 1. Ideal-gas (linear approximation), correlation, and total ground-state energies per volume (in units of $\hbar^2/m\sigma^2$) vs localization parameter α for the Bose hard-sphere fcc crystal at reduced average solid density $\rho_s\sigma^3=0.3$.

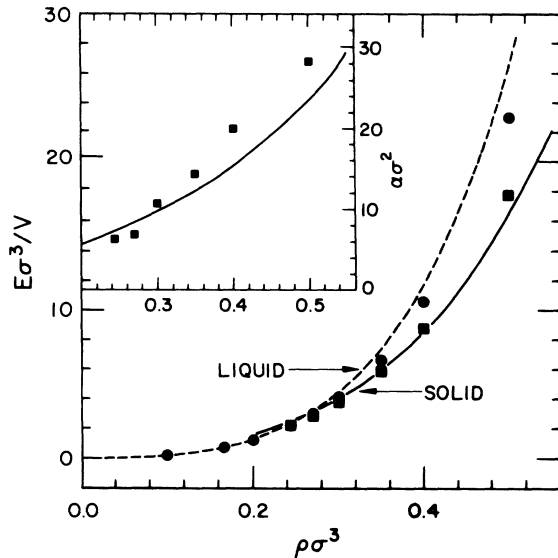


FIG. 2. Total ground-state energies per volume (in units of $\hbar^2/m\sigma^2$) vs density ρ for the Bose hard-sphere liquid (from PPA) and fcc crystal (from MWDA). Circles and squares are simulation data (Ref. 13) for the liquid and crystal phases, respectively. Inset: The density dependence of the localization parameter α .

ergy curve (E/V vs ρ_s) is obtained. The result for the fcc crystal is shown together with the PPA liquid-phase energy curve in Fig. 2, where the crossing of the two curves confirms the occurrence of a freezing transition. Also shown for comparison are the simulation data of Hansen, Levesque, and Schiff¹³ for the liquid and fcc crystal. The inset in Fig. 2 shows the dependence of α on ρ_s , illustrating that an increase in density naturally results in stronger localization. The value of α at the solid coexistence density is directly related to the Lindemann parameter L , defined as the ratio of the rms displacement of an atom from its lattice site to the nearest-neighbor distance in the solid at coexistence. For the fcc crystal, $L = (3/aa^2)^{1/2}$, where a is the lattice constant.

The liquid-solid transition is finally located by constructing a common tangent to the liquid and solid ener-

gy curves, ensuring equality of the pressures and of the chemical potentials in the two phases. The resulting freezing parameters are given in Table I for fcc, hcp,¹⁴ and bcc crystals, together with available simulation data.¹³ Considering the extreme sensitivity of the coexistence densities—as determined by the common tangent construction—to the accuracy of the energies, we view the overall agreement between theory and simulation as quite favorable. The predicted solid and liquid coexistence densities are a little too high, by 14% and 7%, respectively. The predicted *change* in density is significantly higher than the simulation value, but the Lindemann parameter, a quite sensitive test of a freezing theory, is underpredicted by only 11%. This discrepancy, as well as that in the change in energy per particle, can be at least partly attributed to the overprediction of the solid coexistence density.

The Lindemann parameter is of particular significance to the physical nature of the freezing transition. Its value predicted by the MWDA for Bose hard spheres ($L=0.240$, from Table I) is close to 3 times the corresponding prediction for classical hard spheres ($L=0.097$, from Ref. 6), in general agreement with simulation.¹¹ In the theory, the larger quantum value evidently results from the relatively strong variation of the ideal-gas and correlation energies with localization, such that minimization of the total energy occurs at much weaker localization than in the classical system (compare Fig. 1 of this paper with Fig. 2 of Ref. 6).

The choice of crystal structure evidently has only a minor effect, reflecting the fact that the predicted energies of the different structures are extremely close, actually differing by less than 0.5% over the range of densities shown in Fig. 2. Indeed, on the scale of Fig. 2 the energy curves would be practically indistinguishable. The similar behavior of the two close-packed structures is not surprising, since it has previously been seen in simulations^{15,16} of ^4He and of the classical hard-sphere system. The similarity of the bcc structure to the close-packed structures is more interesting, since it is in sharp contrast with the classical case, where both density-functional theory and simulation predict the free energy

TABLE I. Freezing parameters for the Bose hard-sphere system at zero temperature: average solid density ρ_s , liquid density ρ_l , change in density $\Delta\rho$, change in energy per particle $\Delta(E/N)$ (in units of $\hbar^2/m\sigma^2$), Lindemann parameter L , and c/a ratio for the hcp crystal (Ref. 14).

	$\rho_s \sigma^3$	$\rho_l \sigma^3$	$\Delta\rho \sigma^3$	$\Delta(E/N)$	L	c/a
Simulation ^a						
fcc	0.25 ± 0.02	0.23 ± 0.02	0.02	1.28	0.27	
MWDA						
fcc	0.284	0.246	0.038	2.668	0.240	
hcp	0.284	0.246	0.038	2.688	0.240	1.629
bcc	0.280	0.247	0.033	2.338	0.249	

^aSee Ref. 13.

of the bcc crystal to be always significantly higher than that of the fcc near freezing.¹⁷ This may reflect a smaller sensitivity to structure resulting from the larger rms atomic displacements in the quantum solid. To our knowledge, however, there exist no simulation results for freezing of the Bose hard-sphere liquid into a bcc crystal with which this prediction may be compared.

The theory described above appears to be a satisfactory extension of the classical density-functional method to *quantum* freezing. It is important to note, however, that because the predictions of the theory are very sensitive to the input liquid-state structure, i.e., $v(k)$, it is difficult to separate the issue of the accuracy of the theory from the issue of the accuracy of the necessary input. As mentioned, the choice of the PPA $v(k)$ is not completely satisfactory, and scaling to enforce the quantum compressibility rule is necessary to obtain favorable agreement with simulation. Thus, although the theory has been demonstrated to be successful for a particular liquid-state structure (PPA), it is clearly of interest to explore its utility further by using more accurate approximations to the liquid state. This issue, as well as the applicability of the theory to other bulk-phase phenomena, such as solid-solid transitions, and to other systems, such as Fermi hard spheres or—*via* perturbation theory—Lennard-Jones models of ³He and ⁴He, is currently under investigation.

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¹²Two important practical points: First, we computed $\epsilon(\rho)$ and $v(k;\rho)$ at discrete densities and wave vectors in the ranges $0 < \rho\sigma^3 < 0.4$ (at intervals of 0.01) and $0 < k\sigma < 30$ (at intervals of about 0.1) and then simply linearly interpolated between points. Second, for values of a relevant near freezing we find that ten reciprocal-lattice vector shells (a given shell including all vectors of the same magnitude) is quite sufficient to ensure convergence of the sum in Eq. (10).

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¹⁴For the hcp structure, the c/a ratio was treated as an additional variational parameter. Note that its optimum value is very close to the ideal close-packed value $c/a = (8/3)^{1/2}$.

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