Self-Consistent Theory of Freezing of the Classical One-Component Plasma

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A new formulation of the modified weighted density approximation of inhomogeneous classical fluids is presented which is exact to third order in the functional expansion of the excess free energy but includes, approximately, correlations to *all* orders. It requires as input the pair and triplet structure of the uniform liquid, and when applied to the one-component plasma yields results which are in good agreement with simulation data.

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It has been shown [1] that for systems interacting by means of purely repulsive power-law potentials, $\sim r^{-m}$, the change in specific volume Δv on melting approaches zero as $m \rightarrow d$, where d is the dimensionality of the system. When $m \leq d$, the thermodynamic functions are undefined, unless the system is provided with a "uniform neutralizing background," in which case Δv at melting again vanishes [1]. The dense one-component plasma (OCP; $m=1$; ion charge Ze) [2] is a case in point: it freezes under constant *density*, and not under the usual condition of constant pressure [3]. Here we examine the application of density-functional theory (DFT) to this problem of *isochoric* freezing, and propose a new approximation to deal with it.

The excess thermodynamic properties of the OCP depend on a single dimensionless variable, the plasma parameter Γ defined by

$$\Gamma=\beta(Ze)^2/a \quad (\beta=1/k_BT)\,, \tag{1}$$

where a is the "ion-sphere radius" $[(4\pi/3)a^3=\rho^{-1}]$. The crystallization of the OCP into a bcc solid has been the object of extensive simulation work [4] and the best current estimate of the value of Γ at which the freezing transition is observed is $\Gamma_c=178$.

The density-functional approach to crystallization is based on the theorem [5] that the Helmholtz free energy $F[\rho(\mathbf{r})]$ of an inhomogeneous system is a *unique functional* of the one-particle density $\rho(\mathbf{r})$, which in a crystalline solid is extremely inhomogeneous. A widely used version of DFT is that of Ramakrishnan and Yussouff (RY) [6], in which a functional Taylor expansion is made of the excess Helmholtz free energy of the solid, about the density of a uniform liquid, and is usually truncated at second order. This approximation has proven to be reasonably successful in studying the freezing of a hard-sphere liquid [6,7] but so far is unable to predict freezing for a system with a long-ranged interaction, such as the OCP [8]. An alternative self-consistent approach is the modified weighted density approximation (MWDA) [9] based on coarse-graining ideas of Tarazona and others [10], and a straightforward application of this theory to the *isochoric* melting of the classical OCP also fails to predict any freezing, as noted earlier by Zeng and Oxtoby [11]. On the other hand, the MWDA is reported to be successful for the study of quantum freezing of jellium [12]. In the MWDA, as in other functional approaches, the excess Helmholtz free energy of the solid, $F_{\rm ex}[\rho(\mathbf{r})]$, is approximated by that of a *liquid* at a certain weighted density $\hat{\rho}[\rho(\mathbf{r})]$, which is evaluated self-consistently, but in a way that guarantees that the approximate functional $F_{\rm ex}^{\rm MWDA}(\hat{\rho})$ is exact to second order in the RY expansion. The self-consistency requirement in the determination of $\hat{\rho}$ also guarantees that in general there are contributions from *all* higher orders in the functional expansion included in the MWDA functional. Indeed, it can be shown for the MWDA that, *provided* $\Delta v \neq 0$, the third-order contribution to the MWDA functional is nonzero and extensive [13]. However, this result no longer holds for an *isochoric* transition. This can be seen noting that the third-order contribution to $F_{\rm ex}[\rho(\mathbf{r})]$ is given by

$$F_{\rm ex}^{(3)}=-\frac{k_BT}{3!}\int\int\int c_0^{(3)}(\mathbf{r},\mathbf{r}',\mathbf{r}'';\rho)[\rho(\mathbf{r})-\rho][\rho(\mathbf{r}')-\rho][\rho(\mathbf{r}'')-\rho]\,d\mathbf{r}\,d\mathbf{r}'\,d\mathbf{r}''\,, \tag{2}$$

where ρ is the density of the uniform liquid. But if we now use $c_0^{(3)}$ as given in Ref. [13], and take into account the fact that the *average* densities of the solid and the liquid are constrained to be equal in *isochoric* melting, we see that $F_{\rm ex}^{(3)}$ for the MWDA must vanish. A similar conclusion can be drawn for all higher contributions to $F_{\rm ex}^{\rm MWDA}$, so that for an isochoric transition the MWDA is *operationally* equivalent to the original RY theory, truncated at second order. The inability of the MWDA to predict freezing for the OCP is now seen to be predetermined by the condition $\Delta v=0$; for short-ranged interactions the MWDA appears to be adequate, otherwise.

To deal with this difficulty we follow earlier work [9], and write the Helmoltz free energy of the solid as a sum of the "ideal" and the "excess" parts, where the latter is approximated by

$$F_{\rm ex}[\rho(\mathbf{r})]\approx F_{\rm ex}(\hat{\rho})\equiv Nf_0(\hat{\rho}) \tag{3}$$

with f_0 denoting the excess free energy per particle of the *uniform* liquid. The weighted density $\hat{\rho}$ is now constructed from the one-particle density $\rho(\mathbf{r})$ of the solid phase by going beyond MWDA [9] [the first term in (4)] and expanding self-consistently to one higher order; thus we write

$$\hat{\rho}=\frac{1}{N}\int\int w(\mathbf{r}-\mathbf{r}';\hat{\rho})\rho(\mathbf{r})\rho(\mathbf{r}')d\mathbf{r}\,d\mathbf{r}'+\frac{1}{N^2}\int\int\int v(\mathbf{r}-\mathbf{r}',\mathbf{r}-\mathbf{r}'';\hat{\rho})\rho(\mathbf{r})\rho(\mathbf{r}')\rho(\mathbf{r}'')d\mathbf{r}\,d\mathbf{r}'\,d\mathbf{r}''\,, \tag{4}$$

where the sought-for $\hat{\rho}$ appears as an argument in the weight function w, and also in the new weight function v. The weight functions must *both* be normalized [cf. Eq. (12) in Ref. [9]], i.e.,

$$\int w(\mathbf{r}-\mathbf{r}';\hat{\rho})d(\mathbf{r}-\mathbf{r}')+\frac{1}{V}\int\int v(\mathbf{r}-\mathbf{r}',\mathbf{r}-\mathbf{r}'';\hat{\rho})d(\mathbf{r}-\mathbf{r}')d(\mathbf{r}-\mathbf{r}'')=1\,, \tag{5}$$

but, though two functions are connected by a single condition, they can be selected through further approximation by choosing them for a restricted set of possibilities, for example, by requiring that they *separately* satisfy the normalization conditions

$$\int w(\mathbf{r}-\mathbf{r}';\hat{\rho})d(\mathbf{r}-\mathbf{r}')=C\,, \tag{6a}$$

$$\int v(\mathbf{r}-\mathbf{r}',\mathbf{r}-\mathbf{r}'';\hat{\rho})d(\mathbf{r}-\mathbf{r}')=1-C\,, \tag{6b}$$

where C is an arbitrary constant. Equation (6b) imposes a constraint on the function v, namely, that its integral over any of its two arguments must be a constant, independent of the value of the other. A unique specification of w and v follows if we impose the conditions that the second *and* third functional derivatives of the approximate excess free-energy functional of Eq. (3) with respect to the density are, in the uniform density limit, equal to $-k_BT$ times the second- and third-order direct correlation functions of the uniform liquid, respectively. In k space, we then obtain simple expressions for the weight functions w and v, namely,

$$-\beta^{-1}c_0^{(2)}(k;\rho_0)=2f_0'(\rho_0)(1-C)\delta_{k,0}+\rho_0 f_0''(\rho_0)\delta_{k,0}+2f_0'(\rho_0)w(k;\rho_0)\,, \tag{7}$$

found previously [9], and

$$\begin{aligned}-\beta^{-1}c_0^{(3)}(\mathbf{k},\mathbf{k}';\rho_0)=&\left[-6\frac{f_0'(\rho_0)}{\rho_0}+6C\frac{f_0'(\rho_0)}{\rho_0}+3f_0''(\rho_0)-6Cf_0''(\rho_0)+\rho_0 f_0'''(\rho_0)\right]\delta_{k,0}\delta_{k',0}\\&+2f_0''(\rho_0)[w(k;\rho_0)\delta_{k',0}+w(k';\rho_0)\delta_{k,0}+w(k;\rho_0)\delta_{\mathbf{k}+\mathbf{k}',0}]\\&+2f_0'(\rho_0)[w'(k;\rho_0)\delta_{k',0}+w'(k';\rho_0)\delta_{k,0}+w'(k;\rho_0)\delta_{\mathbf{k}+\mathbf{k}',0}]+6f_0'(\rho_0)\frac{v(\mathbf{k},\mathbf{k}';\rho_0)}{N}\,,\end{aligned} \tag{8}$$

where primes denote differentiations with respect to density. For $k=0$, Eq. (7) along with the normalization condition (6a) ensures that the compressibility sum rule,

$$-\beta^{-1}c_0^{(2)}(k=0,\rho_0)=2f_0'(\rho_0)+\rho_0 f_0''(\rho_0)\,, \tag{9}$$

is satisfied [14]. For $k'=0$, Eqs. (6)-(8) all ensure that the sum rule

$$c_0^{(3)}(k,k'=0;\rho_0)=\frac{\partial c_0^{(2)}(k;\rho_0)}{2\rho_0} \tag{10}$$

is satisfied for every k.

To apply this approximate theory, we determine the excess free energy of an OCP bcc solid (reciprocal-lattice vectors $\{\mathbf{G}\}$), add to it the exact ideal part of the free energy, and then minimize with respect to a single variational parameter, namely, the specified localization parameter α of the Gaussians which are taken to model the one-particle density of the solid [15]. Comparison of this minimum with the known liquid free energy will then determine the freezing transition, if it exists. Following Ref. [9] and using Eq. (4) we find for the Gaussian model the self-consistency condition on the requisite $\hat{\rho}$,

$$\hat{\rho}(\rho_s,\alpha)=\rho_s\left[1-\frac{1}{2\beta f_0'(\hat{\rho})}\sum_{\mathbf{G}\neq 0}e^{-G^2/2\alpha}c_0^{(2)}(\mathbf{G};\hat{\rho})-\frac{\rho_s}{6\beta f_0'(\hat{\rho})}\sum_{\mathbf{K}\neq 0}\sum_{\mathbf{Q}\neq 0,-\mathbf{K}}e^{-K^2/4\alpha}e^{-Q^2/4\alpha}e^{-(\mathbf{K}+\mathbf{Q})^2/4\alpha}c_0^{(3)}(\mathbf{K},\mathbf{Q};\hat{\rho})\right]\,, \tag{11}$$

which can in principle be applied to the freezing of any system. For the OCP with average solid density ρ_s we can make use of the fact that $\Gamma\propto\rho^{1/3}$, and reexpress the iteration implied by (11) in terms of a weighted plasma parameter $\hat{\Gamma}$. For the required excess free energy per ion of the liquid phase of the OCP, we adopt the expression of DeWitt, Slattery, and

Stringfellow [4]:

$$\beta f_0(\Gamma)=a\Gamma+\frac{b}{s}\Gamma^s+c\ln\Gamma-\left(a+\frac{b}{s}+d\right), \qquad (12)$$

where $a=-0.8992$, $b=0.596$, $c=-0.268$, $s=0.3253$, and $d=0.4363$. For the required second-order direct correlation function $c_0^{(2)}$, we use the generalized mean spherical approximation (GMSA) of Chaturvedi, Senatore, and Tosi [16], which has the particular advantage of being analytic and which gives results in excellent agreement with simulation data for a wide range of Γ in the strong-coupling regime. Thermodynamic consistency requires that the $k\to 0$ limit of the structure factor $S(k)$ [and hence $c_0^{(2)}(k)$] must be related to the free energy of the system [Eq. (12)] and its derivatives. When approximations to $c_0^{(2)}$ are used, as with the GMSA, consistency can nevertheless still be maintained, and we do this here by following the procedure of Chaturvedi, Senatore, and Tosi [16].

Although the *triplet* structure of uniform liquids is still relatively poorly known in general, several different schemes have recently been developed [17–20] to approximate $c_0^{(3)}$. Here, we present results obtained using two different approximations, namely,

$$c_0^{(3)}(\mathbf{r},\mathbf{r}')=h(r)h(r')h(|\mathbf{r}-\mathbf{r}'|), \qquad (13)$$

which has been introduced by Iyetomi and Ichimaru [17], and

$$c_0^{(3)}(\mathbf{r},\mathbf{r}')=t(r)t(r')t(|\mathbf{r}-\mathbf{r}'|), \qquad (14)$$

introduced by Barrat, Hansen, and Pastore [20]. In (13), $h(r)\equiv g(r)-1$; in (14), the more general function $t(r)$ can be unambiguously determined by using the exact relation (10) between $c_0^{(2)}$ and $c_0^{(3)}$. In both cases, we include contributions from 100 shells in the reciprocal-lattice summation of Eq. (11). The second summation in this equation is performed over "triangles" formed by reciprocal-lattice vectors and, following Ref. [19], we characterize each triangle by the triplet (l,m,n) of indices each numbering a star of the reciprocal-lattice vectors. With approximation (14) used for $c_0^{(3)}$, we sum over the following 28 sets of triangles:

$n=1,\ 1\le l\le 5,\ l\le m\le 11$ [19]

$n=2,\ 2\le l\le 4,\ l\le m\le 9$ [6]

$n=3,\ l=3,\ l\le m\le 5$ [3].

This choice is already sufficient to guarantee convergence of the double summation in Eq. (11), meaning that inclusion of more triangles than those indicated does not change the sum by more than 1% for a Gaussian width parameter $\alpha a^2=12$ at which point the total free energy has a minimum at freezing (Fig. 1). With approximation (13), on the other hand, convergence of the double summation in Eq. (11) is somewhat slower, though ultimately guaranteed by the Gaussian factors. It is known [8,17] that for larger values of its arguments, approximation (13) itself is quite inaccurate, and for this reason we follow Barrat [8] by including only the (1,1,1) and (1,1,2) sets in order to provide a comparison. Figure 1 illustrates the dependence of F, $F_{\rm id}$, and $F_{\rm ex}$ on the localization parameter α with approximations (13) and (14) used for $c_0^{(3)}$. Figure 2 illustrates the dependence of the weighted plasma parameter $\hat{\Gamma}$ on the localization parameter [21] for $\Gamma=180$, again with approximations (13) and (14) used for $c_0^{(3)}$.

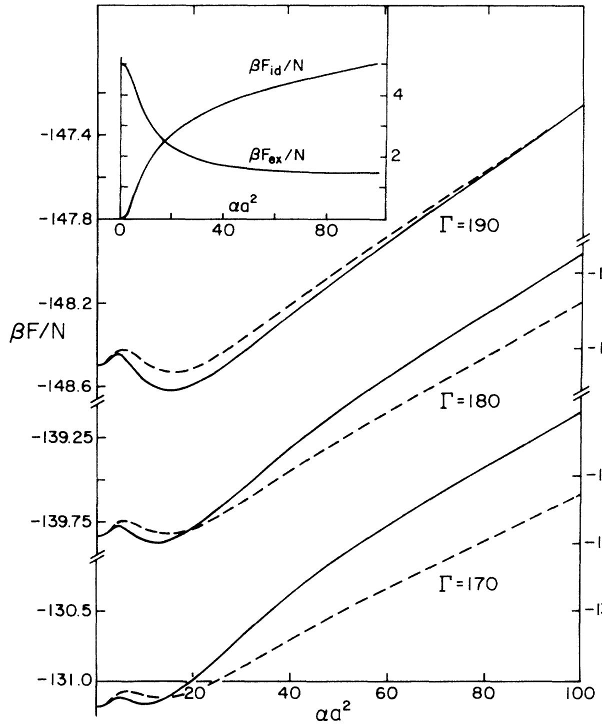

FIG. 1. Total free energy vs localization parameter α for the bcc OCP solid at various coupling constants Γ. The solid line represents results obtained with approximation (14) used for $c_0^{(3)}$, and the dashed line results obtained with approximation (13). Inset: Ideal-gas (favoring delocalization) and excess (favoring localization) free energies for $\Gamma=180$; displayed here are $\beta F_{\rm id}/N$ and $\beta F_{\rm ex}/N-\beta F_{\rm ex}(\alpha=0)/N+5$, where $\beta F_{\rm ex}(\alpha=0)/N=-139.83$ (see below).

Referring to Fig. 1, we find that with approximation (13) freezing occurs at $\Gamma=183$, and with approximation (14) at $\Gamma=176$, both in quite good agreement with simulation data [4]. The Lindemann ratio L and the change of entropy $\Delta S/Nk_B$ upon melting are respectively given by 0.17 and -0.74 with approximation (13) used for $c_0^{(3)}$, and 0.20 and -0.87 with approximation (14). Again, these results are in good agreement with the simulation results, $L=0.17$ and $\Delta S/Nk_B=-0.80$, respectively [2]. *Specific* values of the critical parameters can be quite sensitive to the particular approximation used for the third-order correlation function. In fact, the estab-

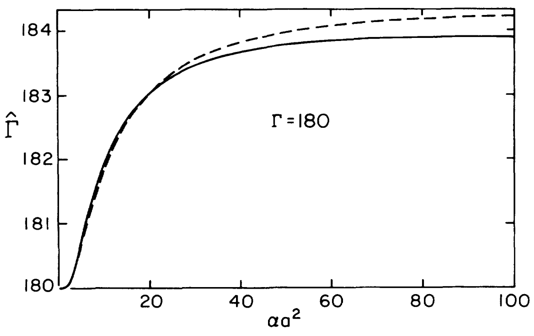

FIG. 2. The weighted plasma parameter $\hat{\Gamma}$ vs localization parameter α for the bcc OCP solid at coupling constant $\Gamma=180$. Solid line: results obtained with approximation (14) used for $c_0^{(3)}$. Dashed line: results obtained with approximation (13) used for $c_0^{(3)}$.

lishment of freezing in a reasonable range of Γ seems to raise itself as a possible test of the quality in which other theories determine the details of $c_0^{(3)}$.

The major point, however, is that as suggested earlier by Barrat [8] explicit inclusion of the three-particle correlation effects appears necessary in order to predict the constant-volume freezing of the OCP, and a more detailed knowledge of the third-order direct correlation function is now clearly of great significance. In particular, the details of $c_0^{(3)}(\mathbf{k},\mathbf{k}')$ which are important to the location of the freezing transition (if it exists) are the values of this function at nonzero wave vectors; the most important are the (1,1,1) and (1,1,2) triangles of reciprocal-lattice vectors for the bcc structure. It is here that the other approximations for $c_0^{(3)}$ are less satisfactory, including the WDA [18] and MWDA [19] themselves. The new approximation is by construction exact to third order in the functional expansion of the excess free energy. The self-consistency requirement between the weight density and the argument of the weight functions again guarantees that in general the new free-energy functional must include, at least approximately, correlations from *all* higher orders. But in exactly the way that the MWDA was shown to be equivalent to a second-order RY expansion for the special case of *isochoric* freezing, so it can be shown that the new approximation is equivalent to a third-order RY theory for such a freezing transition. The practical advantage of inclusion of higher than third-order correlations can therefore be lost when a constraint $\Delta v=0$ is imposed. Nevertheless, it is particularly interesting to note that the third-order correction to the excess free energy is equivalent *in its effect* to an almost complete elimination of the contribution from the [200] star of reciprocal-lattice vectors in the *second-order* theory; this accounts for but does not justify the earlier success of a "truncated" second-order theory [3,22], in which the contribution from this star is arbitrarily omitted. Finally, we reiterate that the approach is a nonperturbative, self-consistent theory of nonuniform classical systems, and can therefore be directly applied to any system described by an inverse power-law potential.

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