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Crystallization of the classical one-component plasma

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A theory of the crystallization of the three-dimensional classical one-component plasma is described. The theory is based on analysis of the nonlinear equation for the inhomogeneous density distribution at phase equilibrium. We report calculations of the plasma parameter $\Gamma \equiv (Ze^2/k_BT)(4\pi\rho/3)^{1/3}$, and the entropy change accompanying the transition. These values are in good agreement with those observed in computer simulations.

A three-dimensional classical one-component plasma (OCP), composed of charges Ze, with density ρ, in a rigid neutralizing continuum background,[1] undergoes a first-order phase transition from a fluid to a body-centered-cubic (bcc) crystal when

$$\Gamma = (Ze^2/k_BT)(4\pi\rho/3)^{1/3} = 171 \pm 3$$

(Ref. 2). Monte Carlo simulations indicate that the entropy change per ion in this transition is $0.82k_B$, that the crystal phase is mechanically stable for $\Gamma \geq 140$, and that the value of the liquid structure factor at the first peak at crystallization is $S(q_m) \simeq 3.0$. Since the neutralizing background of the OCP is rigid there can be no volume change accompanying the transition.[3]

Although there are several reports of the application of integral equation theories to the description of the thermodynamic properties of the OCP,[1] we are aware of no first-principles statistical-mechanical study of the fluid-to-crystal transition. In this Rapid Communication we describe a theory of the freezing of the OCP, based on analysis of the change of solution of the equation for the inhomogeneous density distribution at phase equilibrium. We report the results of two related but distinct calculations. First and, from our point of view, most important, the features of the freezing transition of the OCP are predicted solely from the analysis of the above-mentioned integral equation. This analysis takes the form of a search for the bifurcation point at which the uniform density distribution characteristic of the liquid phase changes to the periodic density distribution characteristic of the crystalline phase. The results of this calculation are in good, but not perfect, agreement with computer simulation data. Second, recognizing that simplifications introduced to enable the bifurcation analysis to be executed can, and do, lead to numerical inaccuracies in the predictions of the theory, we impose the condition of equality of grand potentials of the two phases at the phase transition on an order-parameter representation of the grand potentials of those phases. The order parameters used are the same as appear in the bifurcation analysis, and refer to the amplitudes of the spatial Fourier components of the density distribution in the crystal. This procedure provides values for the plasma parameter at the transition and the entropy change on freezing which are in excellent agreement with the computer simulation values.

Our analysis starts with the following exact expansion[4] for the singlet distribution function as a function of position, $\rho(\vec{R}_1)$, of an inhomogeneous fluid:

$$\begin{aligned}\frac{\rho(\vec{R}_1)}{z} &= \exp\left(\sum_{k=1}^{\infty}\frac{1}{k!}\int S_{k+1}(\vec{R}_1,\ldots,\vec{R}_{k+1})\rho(\vec{R}_2)\cdots\rho(\vec{R}_{k+1})\,d\vec{R}_2\cdots d\vec{R}_{k+1}\right)\\ &\equiv \exp[F(\vec{R}_1,\{\rho(\vec{R}_i)\})] \;,\end{aligned} \tag{1}$$

where $S_{k+1}(\vec{R}_1,\ldots,\vec{R}_{k+1})$ is the sum of all irreducible Mayer cluster diagrams of order $k+1$. The fugacity z is determined by

$$\lim_{V\to\infty}\frac{1}{V}\int d\vec{R}\rho(\vec{R}) = \rho \;, \tag{2}$$

where ρ is the mean density of the system. The argument of the exponential term on the right-hand side of Eq. (1), $F(\vec{R}_1,\{\rho(\vec{R}_i)\})$, is the generating function of the n-particle direct correlation function $c_n(\vec{R}_1,\ldots,\vec{R}_n)$:[5–7]

$$c_n(\vec{R}_1,\ldots,\vec{R}_n) = \frac{\delta^{n-1}F(\vec{R}_1,\{\rho(\vec{R}_i)\})}{\delta\rho(\vec{R}_2)\cdots\delta\rho(\vec{R}_n)} \;. \tag{3}$$

A functional Taylor expansion of this generating function about its liquid-state value $F(\vec{R}_1,\{\rho_l\})$, truncated after the first three terms, leads to

$$\frac{\rho(\vec{R}_1)}{z} = \frac{\rho_l}{z_l}\exp\left(\int d\vec{R}_2 c_2(\vec{R}_{12};\rho_l)\Delta\rho(\vec{R}_2) + \frac{1}{2}\int d\vec{R}_2 d\vec{R}_3 c_3(\vec{R}_1,\vec{R}_2,\vec{R}_3;\rho_l)\Delta\rho(\vec{R}_2)\Delta\rho(\vec{R}_3)\right) \;, \tag{4}$$

where $\Delta\rho(\vec{R})$ is the density difference $\rho(\vec{R})-\rho_l$. In Eq. (4), ρ_l and z_l are the density and the fugacity of the liquid phase.

We now expand the singlet density distribution in a Fourier series and set $\rho(\vec{R}_1) = \rho_s(\vec{R}_1)$:

$$\rho_s(\vec{R}) = \rho_l + \Delta\rho(\vec{R}) = \rho_l(1+\phi_0) + \rho_l\sum_{\vec{G}}\phi_{\vec{G}}\,e^{i\vec{G}\cdot\vec{R}} \;, \tag{5}$$

where the $\{\vec{G}\}$ are the reciprocal-lattice vectors of the crystal, the $\phi_{\vec{G}}$ are expansion coefficients, and ϕ_0 is the fractional density change on freezing. ϕ_0 and $\phi_{\vec{G}}$ are the order parameters for the transitions; they are zero for the liquid phase and nonzero for the crystalline phase. At a first-order phase transition, all or some of these order parameters will undergo a jump discontinuity. As already remarked, ϕ_0 must be zero for the OCP to preserve charge neutrality.

It is worth pointing out that the order-parameter expansion (5) neglects the terms corresponding to shear deformation of the solid, and the corresponding thermal fluctuations. Inclusion of both categories of terms is a nontrivial problem to which we do not have a simple solution at the moment.

We restrict the Fourier expansion of $\rho_s(\vec{R})$ to the appropriate set of first and second reciprocal-lattice vectors.[5] The solution of Eq. (4) then reduces, for the bcc lattice, to the problem of solving the coupled nonlinear equations

$$\begin{aligned} 12\psi_{\vec{G}_\alpha} &= \int_\Delta d\vec{R}\,\xi_{\vec{G}_\alpha}(\vec{R})B(\vec{R}) \Big/ \int_\Delta d\vec{R}\,B(\vec{R}) \;, \\ 24\psi_{\vec{G}_\beta} &= \int_\Delta d\vec{R}\,\xi_{\vec{G}_\beta}(\vec{R})B(\vec{R}) \Big/ \int_\Delta d\vec{R}\,B(\vec{R}) \;, \end{aligned} \tag{6}$$

with

$$\psi_{\vec{G}_\alpha} = \frac{\rho_l}{\rho_s}\phi_{\vec{G}_\alpha}, \quad \xi_{\vec{G}_\alpha}(\vec{R}) = \sum_{\vec{G}_\alpha} e^{i\vec{G}_\alpha\cdot\vec{R}} \;, \tag{6a}$$

$$B(\vec{R}) = \exp[\lambda_{\vec{G}_\alpha}\psi_{\vec{G}_\alpha}\xi_{\vec{G}_\alpha}(\vec{R}) + \lambda_{\vec{G}_\beta}\psi_{\vec{G}_\beta}\xi_{\vec{G}_\beta}(\vec{R})] \;, \tag{6b}$$

$$\tilde{c}_2(\vec{G}_\alpha) = \int d\vec{R}_{12} e^{i\vec{G}_\alpha\cdot\vec{R}_{12}} c_2(\vec{R}_{12};\rho_l) \;, \tag{6c}$$

$$\tilde{c}_3(\vec{G}_\alpha, 0) = \int d\vec{R}_{12} d\vec{R}_{13} e^{i\vec{G}_\alpha\cdot\vec{R}_{12}} c_3(\vec{R}_1, \vec{R}_2, \vec{R}_3;\rho_l) \;, \tag{6d}$$

$$\lambda_{\vec{G}_\alpha} = \rho_s[\tilde{c}_2(\vec{G}_\alpha) + \rho_l\phi_0\tilde{c}_3(\vec{G}_\alpha, 0)] \;, \tag{6e}$$

where Δ, the volume of the unit cell, is defined as $2\rho_s^{-1}$.

Note that a uniform singlet density is always a solution of Eq. (6). However, Eq. (6) is nonlinear, so there can be additional nonuniform solutions. To investigate this possibility we have solved Eq. (6) and searched for bifurcations[5–7] in the pair $(\lambda_{\vec{G}_\alpha}, \lambda_{\vec{G}_\beta})$. At a bifurcation point the fluid phase, characterized by a uniform density, becomes unstable relative to the crystal, characterized by a periodic density distribution.[8] For a two-order-parameter theory, such as we describe, there is a line of bifurcations generated by pairs of values of $\lambda^*_{\vec{G}_\alpha}$ and $\lambda^*_{\vec{G}_\beta}$ (see Fig. 1). The construction of this line for the bcc lattice is described in Ref. 6. Now, along the freezing line $\lambda^*_{\vec{G}_\alpha}$ and $\lambda^*_{\vec{G}_\beta}$ are also related by the consistency conditions[6,7]

$$\begin{aligned} \rho_s^*[\tilde{c}_2(\vec{G}_\alpha) + \rho_l^*\phi_0\tilde{c}_3(\vec{G}_\alpha, 0)] &= \lambda^*_{\vec{G}_\alpha} \;, \\ \rho_s^*[\tilde{c}_2(\vec{G}_\beta) + \rho_l^*\phi_0\tilde{c}_3(\vec{G}_\beta, 0)] &= \lambda^*_{\vec{G}_\beta} \;, \end{aligned} \tag{7}$$

and

$$\frac{\partial}{\partial\rho_s}\lambda_{\vec{G}_\alpha}(\rho_l^*, \rho_s^*) = 0 \;. \tag{8}$$

The consistency conditions (7) are approximate in that Fourier components of c_3 of the form $\tilde{c}_3(\vec{G}_\alpha, \vec{G}_\beta)$ with $\vec{G}_\beta \neq 0$ have been neglected. Condition (8) arises solely from the convexity of the function $\lambda_{\vec{G}_\alpha}$, which is a consequence of the short-range-ordered structure of the OCP liquid for large values of Γ; it singles out the lowest value of ρ_l at which the transition occurs.[5,7]

The implementation of Eqs. (7) and (8) requires detailed information about the liquid structure factor. We have used an analytic theory for the OCP structure factor due to Chaturvedi, Senatore, and Tosi;[9] it is in excellent agreement with the Monte Carlo results of Hansen *et al.*[1] The triplet correlation function $\tilde{c}_3(\vec{G}, 0)$ is calculated by using the rela-

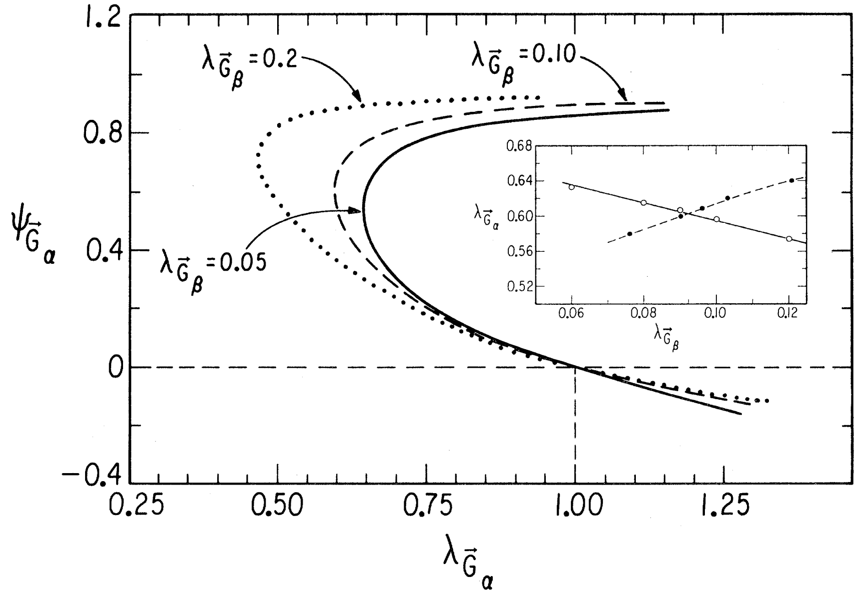

FIG. 1. Two-order-parameter bifurcation curves for the bcc lattice for several values of $\lambda_{\vec{G}_\beta}$. The freezing line generated by the bifurcation pairs $(\lambda^*_{\vec{G}_\alpha}, \lambda^*_{\vec{G}_\beta})$ is shown in the inset. The dashed line in the inset is the solution of the self-consistent condition (8). The intersection of these two lines gives the transition point.

TABLE I. Comparison of predicted and observed properties of OCP crystallization.

ρ_l^*	ρ_s^*	ϕ_0	Γ	$\Delta S/k_B$	Comment
0.2387	0.2411	0.01	144	· · ·	Unmodified bifurcation theory
0.2387	0.2387	0	169.76	1.091	Correction imposed by requirement that both liquid and crystal have equal grand potentials
0.2387	0.2387		171 ±3	0.82	Observed values

tion[10]

$$\tilde{c}_3(\vec{G},0)=\rho_l\frac{\partial}{\partial\rho_l}\tilde{c}_2(\vec{G}) \ . \tag{9}$$

Table I gives the calculated values of ρ_l^*,ρ_s^* and the corresponding value of Γ. The fractional density change on freezing is predicted to be 0.01 which, though very small, contradicts the rigorous result that ϕ_0 must be zero for the OCP. We attribute this nonzero value of ϕ_0 to the approximations in the theory, especially the truncation of the order-parameter expansion and the neglect of $\tilde{c}_3(\vec{G},\vec{G}')$ and higher-order correlation functions. We regard the very small value predicted for ϕ_0 to be supporting evidence for our approach in view of the approximations we have made.

The various approximations in this theory, such as the neglect of higher-order direct correlation functions, higher-order reciprocal-lattice vectors, and shear motion in the crystal,[12] lead to a displacement of the bifurcation point from that at which the approximate grand potentials of the liquid and crystal are equal. To rectify the net effect of these approximations we can impose, as a condition, the equality of grand potentials. Since $c_0\rightarrow\infty$ for the OCP $[c_0\equiv\tilde{c}_2(\vec{G}=0)]$, we take advantage of the fact that ϕ_0 is zero and evaluate the limiting form for the grand potential difference as $c_0\rightarrow\infty$, $\phi_0\rightarrow 0$ but $c_0\phi_0=\alpha$, a constant. It may be shown that

$$\alpha=\ln\left(\Delta/\int_\Delta d\vec{R}\,B(\vec{R})\right) \ , \tag{10}$$

and the equality of grand potentials gives[11]

$$W_s-W_l=0=\rho\alpha+\frac{\rho}{2}\sum_{\vec{G}}\tilde{c}_2(\vec{G})\phi_{\vec{G}}^2+\frac{\rho\Gamma}{6}\sum_{\vec{G}}\left(\frac{\partial}{\partial\Gamma}\tilde{c}_2(\vec{G})\right)\phi_{\vec{G}}^2 \ . \tag{11}$$

With the added constraint of the equality of grand potentials, the predicted onset of freezing is at $\Gamma=169.76$, which is in excellent agreement with the observed value[2] (Table I). The change in entropy per ion on freezing is given by

$$\Delta S=k_B\Gamma\frac{\partial}{\partial\Gamma}(W_s-W_l) \ . \tag{12}$$

We find this value to be $-1.09k_B$, to be compared with the experimental value of $-0.82k_B$, which we regard to be in satisfactory agreement since the neglect of the shear motion of the crystal and of the higher-order direct correlation functions in the description of the OCP fluid should lead to too large a value for $\Delta S/k_B$.

Our analysis of the nonlinear integral equation for the singlet density distribution successfully predicts the freezing transition in the OCP and provides values for the transition parameters that are of modest accuracy. The theory has the advantage of being fully microscopic,[13] in the sense that if carried out exactly equality of the grand potentials of the liquid and crystal, which defines the freezing point, coincides with the point at which the order parameters change discontinuously and the solution of the integral equation for the density bifurcates. However, the approximations we have used, while preserving the qualitative prediction of a first-order phase transition, lead to numerical errors of prediction. The separate imposition of equality of grand potential is a convenient way to correct the numerical inaccuracy of our predictions, but it does represent a departure from the purely microscopic point of view we prefer.

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