Comment on the thermodynamics of a classical one-component plasma

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A variational method used recently in the theory of liquid metals and screened Coulomb systems is extended to treat the thermodynamic properties of a classical, uniform, one-component plasma. The Helmholtz free energy and corresponding thermodynamic derivatives can all be expressed in concise parametric form as functions of an equivalent hard-sphere packing function. The results are generally found to agree well with recent Monte Carlo calculations, especially at temperatures close to the observed crystallization temperature.

Ross and Seale have recently shown that the thermodynamic properties of a classical fluid of particles interacting through a screened Coulomb potential may be accurately calculated via a simple variational method. Similar methods have also been applied earlier, and with considerable success, to Lennard-Jones $r^{-6}$, $r^{-2}$, and $r^{-12}$ potentials, as well as to liquid metals and liquid-metal alloys. In this note we wish to point out that the same analysis can be extended to treat a true (unscreened) Coulomb plasma, that is, a classical fluid of charged particles interacting through a bare Coulomb pair-wise potential and placed in a uniform compensating background of opposite charge. Although this special case is to some extent implicit in the work of Ross and Seale, it is of such interest, both intrinsically and in its astrophysical application, that it merits direct attention. Moreover, as will be shown below, the various thermodynamic functions can all be expressed in strikingly simple parametric form.

The basis of the variational approach is the so-called Gibbs-Bogolyubov inequality which relates the Helmholtz free energy of a system of particles with pair-wise interactions to that of a suitable isochoric reference system, usually chosen to be an assembly of hard spheres. For the one-component plasma, the inequality takes the form

$$f \leq -T \overline{S} + \frac{1}{4\pi^2} \int_0^\infty k^2 \, dk \left\{ \overline{\varepsilon}(k) - 1 \right\} (4\pi Z^2 \rho^2 / k^2).$$

Here $f$ represents the excess free energy per particle for the Coulomb plasma, that is, the deviation of the free energy per particle from its ideal-gas value; $\overline{S}$ is the excess entropy per particle of the hard-sphere reference fluid; $\overline{\varepsilon}(k)$ is the structure factor of the hard-sphere fluid, and $T$ is the absolute temperature. The first term on the right-hand side is the total excess free energy per particle of the hard-sphere reference fluid, a system of particles interacting as hard spheres having zero potential energy.

A lowest upper found to $f$ can now be obtained simply by minimizing the right-hand side of (1) with respect to the hard-sphere diameter $a$, or equivalently, the packing fraction $\eta = (\pi/6)(N/V)a^3$, of the underlying reference system. For the case of the one-component plasma, the minimization can essentially be carried out analytically. In what follows it will be shown that the resulting variationally determined free energy (and corresponding thermodynamic functions) is in reasonable accord with the analogous quantities determined from computer experiments.

To carry out the minimization, we note that the excess entropy $\overline{S}$ can be obtained from the hard-sphere equation of state via integration of the appropriate Maxwell relation. Choosing the Carnahan-Starling equation of state, which reproduces the Monte Carlo hard-sphere results extremely well, we obtain

$$\overline{S} = -k_B \eta (4 - 3\eta)/(1 - \eta)^2.$$  \hspace{1cm} (2)

The last term in (1) is recognized as the Madelung energy per particle, $e_M$, for a system of point particles distributed according to the hard-sphere structure factor $\overline{S}(k)$. If we take for the latter the Percus-Yevick structure factor, which is available analytically, then the entire integral can be evaluated in closed form, as was first shown by Jones. The result is

$$e_M = -\alpha (Z^2 \rho^2 / 2r_{M5}),$$  \hspace{1cm} (3a)

where

$$\alpha = 6\pi^{2/5} \frac{1 - \eta/5 + \eta^2/10}{1 + 2\eta}$$  \hspace{1cm} (3b)

is the Madelung constant and the Wigner-Seitz radius $r_{M5}$ is defined by $(4\pi/3)r_{M5}^3 = V/N$. It is of
interest to note that at \( \eta = \pi/3\sqrt{2} = 0.74048 \), which is the packing fraction of a close-packed solid, Eq. (3) gives \( \alpha = 1.79048 \), whereas the well-known result for a face-centered-cubic crystal is \( \alpha = 1.7917 \). For the (unphysical) value \( \eta = 1 \), Eq. (5) gives \( \alpha = 1.8 \), which is the Madelung constant appropriate to a point positive charge immersed in a sphere of uniform compensating negative charge.

Using Eqs. (2) and (3) for \( \Sigma \) and \( e_{\mathbf{u}} \), we may readily find the value of \( \eta \) which minimizes the right-hand side of Eq. (1) at fixed temperature \( T \). It satisfies

\[
k_B T = \frac{Z^2 e^2}{2 r_{WS}} \eta^{-1/3} \frac{2 + \eta}{2 - \eta} \frac{(1 - \eta)^3}{(1 + 2\eta)^2}
\]

or

\[
\Gamma = 2\eta^{1/3} \frac{2 - \eta}{2 + \eta} \frac{(1 + 2\eta)^2}{(1 - \eta)^3},
\]

where \( \Gamma = (Z^2 e^2/r_{WS})/k_B T \) is the conventional scaled parameter for the plasma. Equation (4) is plotted in Fig. 1. At \( \Gamma = 155 \), which according to the Monte Carlo results of Pollock and Hansen it represents the freezing point of the plasma, \( \eta = 0.52 \) \( [\sigma = 0.998(V/N)^{1/3}] \). This may be compared to the value \( \eta = 0.492 \) \( [\sigma = 0.980 - 0.982(V/N)^{1/3}] \) at which a liquid of hard spheres solidifies.

Substitution of (4) into (1) yields immediately the minimum free energy \( f(\eta) \) as

\[
f(\eta) = \frac{Z^2 e^2}{2 r_{WS}} \eta^{1/3} \frac{2 + \eta}{2 - \eta} \frac{(1 - \eta)^3}{(1 + 2\eta)^2}
\]

\[
\times \left[ \frac{2 + \eta}{2 - \eta} \frac{(4 - 3\eta)(1 - \eta)^3}{1 + 2\eta} - 6 \left( \frac{\eta}{5} + \frac{\eta^2}{10} \right) \right].
\]

The quantity of principal interest, of course, is the excess free energy as a function of \( \Gamma \). But this relation is readily obtained by combining (5) \{i.e., \( f(\eta) \) and (4) \( \eta(\Gamma) \}; the resulting curve \( f(\eta) \) is shown in Fig. 2 and compared there with the Monte Carlo results of Hansen. Evidently the error in (5) is quite small, especially at large \( \Gamma \); for \( \Gamma = 155 \) it amounts to only \( \sim 1\% \). It could be argued that this excellent agreement is to be expected since most of the free energy, especially at low temperatures, is contributed by the Madelung term which is approximately the same for any liquid, whether hard sphere or Coulombic. Yet even if one compares the temperature-dependent part of \( f \) \{i.e., the deviation of \( f \) from its static-lattice value\} with the corresponding Monte Carlo quantities, the agreement at large \( \Gamma \) is still within \( 20\% \).

We have also plotted in Fig. 2 the excess free energy per particle as calculated within the Debye-Hückel approximation which, as Mermin has shown, gives a rigorous lower bound to \( f \). The lower bound may be seen to be most useful at high temperatures. The present results give an approximate upper bound (approximate by virtue of the Percus-Yevick structure factors used to evaluate the Madelung energy) which is most accurate at low temperatures; they complement therefore the Debye-Hückel bounds.

Given the minimum free energy, it is a straightforward matter to compute other thermodynamic functions. For example, the excess entropy is given by

\[
\bar{s} = -k_B \left[ \frac{\partial}{\partial T} f(T, V, \eta(T))_{r,v} + \frac{\partial n}{\partial T} \frac{\partial}{\partial n} f(T, V, \eta(T))_{r,v} \right].
\]

![FIG. 1. Values of \( \eta \) which minimize the Helmholtz free energy at various values of \( \Gamma \), from Eq. (4).](image)

![FIG. 2. Excess free energy per particle versus \( \Gamma \), as obtained variationally by combining Eq. (4) and (5). For comparison the Monte Carlo results of Hansen and the Debye-Hückel lower bound are also plotted.](image)
But \( \frac{d\eta}{dT} = 0 \) (by the minimum principle) and so \( \overline{\xi} \) is found by taking only an explicit derivative of \( f(T, V, \eta(T)) \) with respect to \( T \). It is, in fact, equal to the hard-sphere excess entropy \( \overline{\xi}(\eta) \). Similarly, the excess specific heat per particle at constant volume is

\[
\Delta c_v = T \left( \frac{\partial \overline{\xi}}{\partial T} \right)_V = \frac{\partial \overline{\xi}}{\partial \ln T} \frac{\partial \ln T}{\partial \eta} ,
\]

or

\[
\frac{\Delta c_v}{k_B} = \frac{2(2-\eta)}{(1-\eta)^3} \left( \frac{1}{3\eta} - \frac{1}{2+\eta} - \frac{1}{2-\eta} + \frac{5}{1-\eta} + \frac{4}{1+2\eta} \right) .
\]

which, combined again with (4), gives \( \Delta c_v \) as a function of \( \Gamma \), a result plotted in Fig. 3. Agreement with the Monte Carlo results\(^1\) is again satisfactory.

As a further example, we note that the equation of state can be determined, within the present approximation, in simple parametric form. The excess pressure \( \Delta p \) satisfies

\[
\Delta p = -N \left[ \frac{\partial f(T, \eta)}{\partial V} \right] \overline{\xi}(\eta)
\]

\[
= -\frac{2}{2\pi} \frac{\pi}{N^2} \frac{1}{\eta^2} \frac{1}{1+\eta/10} .
\]

Once again, the variational principle eliminates the term in \( \Delta p \) involving \( \partial f / \partial \eta \). While \( \Delta p \) is negative, the total pressure, when augmented by the ideal-gas term and by the contribution of the background, will be positive for a realistic plasma.

From these results, we conclude that the variational method is a simple yet numerically reasonable procedure for determining the thermodynamic functions of a one-component plasma. The method is most accurate at moderately low temperatures where computer methods converge most slowly. In this region fluctuations in the potential energy are small compared to the mean potential energy itself.

It is possible to obtain an order-of-magnitude estimate of these fluctuations as follows. The distance of closest approach between two particles in the plasma is \( \sigma \). The corresponding fluctuation \( \Delta r \) approximately satisfies the relation

\[
E(\sigma - \Delta r) - E(\sigma) = \frac{\pi}{3} \sigma^3 T ,
\]

where \( E(\sigma) = Z^2 e^2 / r \). From this it follows that \( \Delta r / \sigma \sim (3/\Gamma)^{1/3} \), which is indeed smallest at large \( \Gamma \).

Note that the success of the variational method does not require that the ratio of mean potential to mean kinetic energy be small, but only that the fluctuations in potential energy be small. Nor does it depend on any similarity between the actual Coulomb interactions in the plasma and those of the hard-sphere reference system. The simplicity of the approach suggests the possibility of extending it to Coulomb mixtures for which Monte Carlo calculations have not been carried out. One intriguing question is the possibility of phase separation in such systems. Phase separation is believed to take place in screened Coulomb mixtures such as may be present in the interiors of the giant planets.\(^1\) Its occurrence in Coulomb mixtures would depend on the precise nature of the neutralizing background. The variational method is probably not sufficiently accurate, however, to allow a calculation of the melting curves of such systems.

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9H. Jones, J. Chem. Phys. 55, 2640 (1971). The result is misprinted in the original; it is correctly given in Eq. (6).


