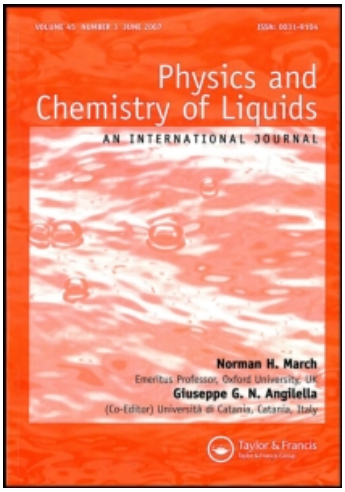

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Letter

Entropy and Pressure of a Liquid with a Charged-Hard-Sphere Reference System

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The Gibbs–Bogoliubov variational method is applied to a simple liquid using a charged-hard-sphere system as a reference system. Simple expressions are derived for the entropy and the pressure.

Recently much attention has been focused on the system of charged hard spheres in a uniform neutralising background (hereafter referred to as the CHS system). The CHS system is characterised by two parameters, the packing fraction $\eta = (\pi/6)n\sigma^3$ and the plasma parameter $\Gamma = (Ze)^2/ak_BT$ where n is the number density, σ the diameter of the hard sphere, Ze the charge of the hard sphere and a is the ion-sphere radius defined by $a = (\frac{4}{3}\pi n)^{-1/3}$. The CHS system is considered as the intermediate system between the hard-sphere (HS) system and the classical one-component plasma (OCP), because the CHS system reduces to the HS system when $\Gamma = 0$ and to the OCP when $\eta = 0$.

Since the analytic expressions for the direct correlation function and the excess internal energy of the CHS system were obtained by Palmer and Weeks[1] in the mean spherical approximation, this system can be considered as one of the useful reference systems. In fact, the CHS system has been used recently to discuss the structural and the thermodynamic properties of the liquid metals and the OCP. Very recently Hoshino[2] derived the expression for the entropy of the CHS system from the analytic expression of the excess internal energy given by Palmer and Weeks[1] and discussed com-

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paratively the entropies of the HS system, the CHS system and the OCP by applying them to liquid alkali metals. In this paper we obtain the expressions for the entropy and the pressure of a real system in the Gibbs–Bogoliubov variational method using the CHS system as a reference system.

The Helmholtz free energy per ion of the CHS system can be written as[2]

$$F_0 = \tfrac{3}{2}k_B T + V_0 - TS_0 = F_{\mathrm{HS}} + F^{\mathrm{ch}} \tag{1}$$

where F_{HS} is the Helmholtz free energy of the HS system, F^{ch} the excess part due to charge, V_0 the potential energy and S_0 the entropy. More explicit expressions for F_{HS} and F^{ch} are as follows:

$$F_{\mathrm{HS}} = \tfrac{3}{2}k_B T - T(S_{id} + S_\eta), \tag{2}$$

$$F^{\mathrm{ch}} = V_0 - TS^{\mathrm{ch}} \tag{3}$$

and

$$S_0 = S_{id} + S_\eta + S^{\mathrm{ch}} = S_{\mathrm{HS}} + S^{\mathrm{ch}}, \tag{4}$$

where S_{id} is the ideal gas term, S_η the packing term and S^{ch} the excess contribution due to charge.[2]

We consider a real system with the same density and atomic mass as those of a reference system, but with different interaction. We assume that the potential energy of the real system can be described by the pairwise interaction

$$V = \frac{1}{2}\sum_{i,j} v(r_{ij}) \tag{5}$$

and that $v(r)$ is independent of temperature. According to the Gibbs–Bogoliubov variational method, the Helmholtz free energy per ion of the real system can be written as

$$F = F_0 + \langle V\rangle_0 - V_0, \tag{6}$$

where $\langle\ \rangle_0$ means the average over the reference system and explicitly we have

$$\langle V\rangle_0 = \frac{1}{2}n\int \mathrm{d}\mathbf{r} v(r) g_0(r/a, \eta, \Gamma), \tag{7}$$

$g_0(r/a, \eta, \Gamma)$ being the radial distribution function of the CHS system. Using (1), (2) and (3), we can rewrite (6) as

$$F = F_{\mathrm{HS}} - TS^{\mathrm{ch}} + \frac{1}{2}n\int \mathrm{d}\mathbf{r} v(r) g_0(r/a, \eta, \Gamma). \tag{8}$$

In (6), the optimum values of η and Γ are found from the Gibbs–Bogoliubov conditions:

$$\left(\frac{\partial F}{\partial \eta}\right)_{T,n,\Gamma} = 0 \tag{9}$$

and

$$\left(\frac{\partial F}{\partial \Gamma}\right)_{T,n,\eta} = 0. \tag{10}$$

Using (8), (10) is written explicitly as

$$-T\left(\frac{\partial S^{\mathrm{ch}}}{\partial \Gamma}\right)_{T,n,\eta} + \frac{1}{2}n\int \mathrm{d}\mathbf{r} v(r)\left(\frac{\partial g_0(r/a,\eta,\Gamma)}{\partial \Gamma}\right)_{T,n,\eta} = 0. \tag{11}$$

Under these circumstances, the entropy of the real system is obtained as follows:

$$\begin{aligned} S &= -\left(\frac{\partial F}{\partial T}\right)_n \\ &= -\left(\frac{\partial F}{\partial T}\right)_{n,\eta,\Gamma} - \left(\frac{\partial F}{\partial \eta}\right)_{T,n,\Gamma}\left(\frac{\partial \eta}{\partial T}\right)_n - \left(\frac{\partial F}{\partial \Gamma}\right)_{T,n,\eta}\left(\frac{\partial \Gamma}{\partial T}\right)_n. \end{aligned} \tag{12}$$

The second and the third terms vanish by (9) and (10) and, using (8), the first term gives

$$\begin{aligned} S = S_{\mathrm{HS}} + S^{\mathrm{ch}} &+ T\left(\frac{\partial S^{\mathrm{ch}}}{\partial T}\right)_{n,\eta,\Gamma} \\ &- \frac{1}{2}n\int \mathrm{d}\mathbf{r} v(r)\left(\frac{\partial g_0(r/a,\eta,\Gamma)}{\partial T}\right)_{n,\eta,\Gamma}. \end{aligned} \tag{13}$$

Noting the relation $T(\partial/\partial T)_{n,\Gamma,\eta} = -\Gamma(\partial/\partial\Gamma)_{n,T,\eta}$ the third term in (13) cancels the fourth term by (11). Similar cancellation was found for the OCP by Young.[3] Therefore the final result is given by

$$S = S_{\mathrm{HS}} + S^{\mathrm{ch}} = S_0. \tag{14}$$

That is, the entropy of the real system is given by the expression for the reference system with the optimum values of η and Γ, given by (9) and (10), inserted. Similar conclusions have been obtained by Edwards and Jarzynski[4] for the HS system, by Young[3] for the OCP and by Gray and Young[5] for the inverse power potential system.

We can also obtain a simple expression for the pressure. We have

$$\begin{aligned} p &= n^2\left(\frac{\partial F}{\partial n}\right)_T \\ &= n^2\left\{\left(\frac{\partial F}{\partial n}\right)_{T,\eta,\Gamma} + \left(\frac{\partial F}{\partial \eta}\right)_{T,n,\Gamma}\left(\frac{\partial \eta}{\partial n}\right)_T + \left(\frac{\partial F}{\partial \Gamma}\right)_{T,n,\eta}\left(\frac{\partial \Gamma}{\partial n}\right)_T\right\}. \end{aligned} \tag{15}$$

The second and the third terms vanish because of (9) and (10) and therefore we obtain, by substituting (8) into (15), the pressure as

$$\begin{aligned} p &= n^2\frac{\partial}{\partial n}\left(F_{\mathrm{HS}} - TS^{\mathrm{ch}} + \frac{1}{2}n\int \mathrm{d}\mathbf{r}v(r)g_0(r/a,\eta,\Gamma)\right)\Bigg|_{T,\eta,\Gamma} \\ &= nk_BT - \frac{1}{2}n^2\int \mathrm{d}\mathbf{r}\left(\frac{r}{3}\frac{\partial v}{\partial r} - n\frac{\partial v}{\partial n}\right)g_0(r/a,\eta,\Gamma). \end{aligned} \tag{16}$$

This is the exact equation of state[6] for the system described by the interaction (5) but modified in that the exact radial distribution function is replaced by the reference one. Similar conclusions have been obtained by Watabe and Young[7] for the HS system, by Young[3] for the OCP and by Gray and Young[5] for the inverse power potential system.

So far we have ignored the configuration independent energy $U(n)$ which is important when we discuss the thermodynamic properties of metals. It is, however, straightforward to include it in the above equations. The entropy (14) does not change, while the pressure (16) is modified by the addition of a term $n^2(\mathrm{d}U(n)/\mathrm{d}n)$ to the right-hand side.

It is straightforward to extend the above discussion to the binary charged-hard-sphere system. The entropy of the binary charged-hard-sphere system has been calculated for some molten salts by Abernethy and Silbert[8] and for the liquid CsAu system by Hoshino[9] on the basis of the analytic solution in the mean spherical approximation.[10–13]

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