

## Thermodynamics of liquid metals: The hard-sphere versus one-component-plasma reference systems

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We have calculated the Helmholtz free energy of liquid Na and Al using a variational principle based on the Gibbs-Bogolyubov inequality in conjunction with hard-sphere and one-component-plasma reference systems. For liquid Na, the one-component plasma gives a lower variational bound to the free energy and fits the experimental structure factor better than does the hard-sphere fluid, in agreement with the findings of Ross *et al.* for liquid Li. Liquid Al, however, is better described by the hard-sphere reference system when exchange-correlation corrections to the pair potential are properly included. We ascribe the difference to the fact that the pair potentials of Al are relatively stiff, and those of the alkali metals relatively soft at small separations.

### I. INTRODUCTION

The thermodynamic properties of liquid metals are frequently studied by hard-sphere perturbation theory.<sup>1</sup> In this approach one expresses the Helmholtz free energy  $F$  of a liquid metal in terms of the free energy  $F_0$  of a reference system, namely, a liquid in which the ions interact like a hard sphere, plus a perturbation term  $\langle V \rangle_0$ .  $\langle V \rangle_0$  is the difference between the Hamiltonians of the real and reference systems evaluated with respect to the distribution functions of the latter. The sum  $F_0 + \langle V \rangle_0$  is then an upper bound to  $F$  and this permits the development of a variational principle in which the hard-sphere diameter is the variational parameter.

The widespread use of the hard-sphere variational technique for liquid metals is due to several factors. First, the hard-sphere approach has been shown (by careful comparison with exact machine simulations) to be very successful in studies of Lennard-Jones liquids such as Ar,<sup>2</sup> which have potentials quite similar (at least in their repulsive cores) to those of liquid metals. Secondly, the experimental liquid-metal structure factors are well approximated in many cases by the hard-sphere

structure factor as calculated in the Percus-Yevick approximation.<sup>3</sup> Moreover, the free energy of the hard-sphere reference system is available analytically as a fit to an exact machine calculation.<sup>4</sup> And finally, there does not exist any other potential reference system for which the free energy and structure factor are available in such a convenient closed form. This last feature is essential for the extensive applications of the method in variational studies of liquid-metallic systems.

In this paper we report the results of a comparison of the variational method as applied to liquid metals with a hard-sphere (HS) reference system and a reference system consisting of a one-component plasma (OCP). This latter is a liquid of point positive ions interacting via a pure Coulomb potential in a uniform negative background. While the thermodynamic properties of this reference system are not available analytically, very good fits to the machine data<sup>5</sup> are available for the free energy, and the tabulated Monte Carlo structure factor<sup>5</sup> is in excellent agreement with the predictions of the hypernetted-chain (HNC) approximation.<sup>6</sup> The execution of the variational principle is thus nearly as convenient as for the hard-sphere case.

Our work has been motivated by the recent ob-

servation of Ross *et al.*<sup>7</sup> that the OCP reference system gives rise to a better (that is, lower) variational upper bound to the free energy than does the HS model, and is in better agreement with simulations for a model of liquid Li. This work calls into question the widespread use of HS modeling for quantitative studies of simple liquid metals, especially in view of the earlier results of a similar comparison between the HS and OCP reference systems as applied to the screened OCP.<sup>8</sup> Since the calculations of Ross *et al.* did not take into account exchange-correlation corrections to the ion-ion potential, and since these are well known to be of prime importance in determining the short-range behavior of this potential,<sup>9,10</sup> we have carried out an additional series of calculations to confirm or refute the superiority of the OCP as a reference system relative to the HS. We find that the role of exchange-correlation corrections to the ion-ion interaction does indeed substantially alter the comparison. For the alkali (Na) the OCP reference system still leads to a lower free energy than does the HS, in agreement with the result of Ross *et al.* for Li. It also provides a better fit to the experimental structure factor. For the polyvalent metals (Al), however, the HS remains the better reference system on both counts when exchange and correlation are properly included. The distinction between monovalent and polyvalent metals is in the repulsive cores, which are stiffer for the polyvalent metals than for the alkalis.<sup>9</sup>

In view of the availability of large machines for Monte Carlo calculations, it might be asked what the necessity is for making a variational calculation at all. But full thermodynamic calculations are not so easily achieved by computer simulation. The main difficulty lies in the calculation of the free energy itself. This requires a thermodynamic integration over a wide density range. Since most simulations are restricted to averaging over a micro-canonical or canonical ensemble, and since the effective ion-ion potential is very sensitive to the density, the free energy of a realistic model liquid metal is quite difficult to obtain in this way. A reference system with a reasonable resemblance to a liquid metal is thus something which potentially has a considerable amount of utility.

The remainder of this paper is organized in the following way. In Sec. II we review the formalism necessary to carry out a variational calculation. Section III presents the results of applications to liquid Na and Al. A brief discussion follows in Sec. IV.

## II. FORMALISM

Since the model Hamiltonian used in our study has been used and discussed extensively<sup>1</sup> in the literature, only a brief summary will be presented here for completeness. One begins with a two-component interacting plasma with  $N$  ions of valence  $Z$  and  $NZ$  electrons in a volume  $\Omega$ . Then the Hamiltonian for the system is

$$\mathcal{H} = \sum_i \frac{p_i^2}{2m} + \frac{1}{2} \sum_{i \neq j} \frac{e^2}{|\vec{r}_i - \vec{r}_j|} + \sum_l \frac{P_l^2}{2M} + \frac{1}{2} \sum_{l \neq l'} W(\vec{R}_l - \vec{R}_{l'}) + \sum_{l,l'} V_{ps}(\vec{r}_l - \vec{R}_{l'}), \quad (1)$$

where  $\{r_i\}$  and  $\{R_l\}$  denote electronic and ionic coordinates,  $\{p_i\}$  and  $\{P_l\}$  the corresponding momenta,  $m$  and  $M$  the masses,  $W(R) = Z^2 e^2 / R$  is the bare ion-ion interaction, and  $V_{ps}$  is the electron-ion pseudopotential which we take to be local and energy independent.

$\mathcal{H}$  is reduced to the "standard" model Hamiltonian widely used in studies of model liquid metals via an application of the adiabatic approximation and many-body perturbation theory in which the electron-ion interaction is retained to second order and electron-electron interactions to all orders by use of the static electron dielectric function  $\epsilon(k)$ . The result is

$$\mathcal{H} = \mathcal{H}_{eg} + \sum_l \frac{P_l^2}{2M} + NE_0 + \mathcal{H}_s, \quad (2)$$

$$\mathcal{H}_s = \frac{N}{2\Omega} \sum_{k \neq 0} \frac{4\pi Z^2 e^2}{k^2} [S(k) - 1] + \frac{N}{2\Omega} \sum_{k \neq 0} \left[ \frac{V_{ps}(k)}{(4\pi Z e^2 / k^2)} \right]^2 \left[ \frac{1}{\epsilon(k)} - 1 \right] S(k). \quad (3a)$$

$V_{ps}(k)$  is the Fourier transform of the pseudopotential and  $\Omega$  is the volume of the liquid metal. The first three terms in (2) are, respectively, the electron gas Hamiltonian, the kinetic energy of the ions, and the  $k=0$  terms omitted from the summation in  $\mathcal{H}_s$ .  $S(k)$  is the ionic structural factor and  $\mathcal{H}_s$  contains the part of the Hamiltonian which depends on the relative ionic configurations.  $\mathcal{H}_s$  now describes an effective one-component classical system interacting with a density-dependent pair potential.

In order to evaluate the last term in (3) we will use the empty core pseudopotential<sup>11</sup>

$$V_{ps} = -\frac{4\pi Ze^2}{k^2} \cos kr_c \quad (3b)$$

and the Lindhard approximation<sup>12</sup> for  $\epsilon(k)$  with and without exchange and correlation corrections.<sup>13</sup> The Helmholtz free energy per ion is then approximated as

$$F = N^{-1}U_0 + E_{kin} - T\mathcal{S}_{ion} + \frac{1}{2\Omega} \sum_{k \neq 0} [S(k) - 1]\Phi(k), \quad (4)$$

where  $\Phi(k)$  is the Fourier transform of the effective interaction between ions,  $U_0$  is the sum of all structure-independent terms,  $\mathcal{S}_{ion}$  is the entropy of the ions and  $E_{kin} = \frac{3}{2}k_B T$  is the kinetic energy per ion.

Upper bounds to the free energy of the model system can now be obtained by an application of the Gibbs-Bogolyubov inequality<sup>14</sup>

$$NF \leq NF^0 + \langle \Phi - \Phi^0 \rangle_{\Phi^0}, \quad (5)$$

where  $F^0$  and  $\Phi^0$  refer to the reference system in which the ions interact via a pair potential  $\Phi^0(R)$ . We need only consider the structure-dependent part of the excess free energy  $F_s [F_s = F - (N^{-1}U_0 + E_{kin})]$  using HS and OCP as reference systems,

$$F_s \leq F_s^0 + E_M + E_{BS}. \quad (6)$$

For the HS reference system,<sup>1</sup> (in units of Ry/ion)

$$F_s^0(\eta) = \frac{4\eta - 3\eta^2}{(1-\eta)^2} k_B T, \quad (7)$$

$$E_M(\eta) = -2\pi Z^2 d^2 \rho \left[ 1 - \frac{\eta}{5} + \frac{\eta^2}{10} \right] / (1+2\eta), \quad (8)$$

$$E_{BS}(\eta) = \frac{2Z^2}{\pi} \int_0^\infty \cos^2 kr_c S_{HS}(\eta; k) \times \left[ \frac{1}{\epsilon(k)} - 1 \right] dk, \quad (9)$$

where  $\eta = \pi d^3 / (6\rho)$  is the packing fraction with  $d$  and  $\rho$  the hard-sphere diameter and number density, respectively.  $E_M$  and  $E_{BS}$  are the Madelung and the band-structure energies as calculated using HS structure factors.  $r_c$  is the empty core radius for the electron-ion pseudopotential and  $S_{HS}(\eta, k)$  is the hard-sphere structural factor in the Percus-Yevick approximation. For a given number density  $\rho$  the packing fraction  $\eta$  is varied to obtain a minimum variational upper bound for the free en-

ergy  $F_s$ .  $E_{BS}(\eta)$  is evaluated numerically.

For the OCP reference system we use a recent four-parameter<sup>15</sup> fit to the free energy of very accurate machine simulations,

$$F^0(\Gamma^0) = k_B T \{ a\Gamma^0 + 4[b(\Gamma^0)^{1/4} - c(\Gamma^0)^{-1/4}] + d \ln \Gamma^0 - [a + 4(b-c)] - 0.420 \}, \quad (10)$$

$$E_M(\Gamma) = k_B T \left[ \frac{\Gamma - \Gamma^0}{\Gamma^0} \right] \times [a\Gamma^0 + b(\Gamma^0)^{1/4} + c(\Gamma^0)^{-1/4} + d], \quad (11)$$

$$E_{BS}(\Gamma^0) = \frac{2Z^2}{\pi} \int_0^\infty \cos^2 kr_c S_{OCP}(\Gamma^0; k) \times \left[ \frac{1}{\epsilon(k)} - 1 \right] dk, \quad (12)$$

where  $a$ ,  $b$ ,  $c$ , and  $d$  are  $-0.89752$ ,  $0.94544$ ,  $0.17954$ , and  $-0.80049$ , respectively. Note that  $E_M(\Gamma)$  in this case is the *deviation* of the Madelung energy from its value in the reference system of plasma parameter  $\Gamma_0$ . The plasma parameter  $\Gamma = (Ze)^2 / (\sigma k_B T)$  where  $\sigma = [3 / (4\pi\rho)]^{1/3}$  is the radius of an average Wigner-Seitz cell surrounding an ion in the liquid. For the structure factor we have solved numerically the hypernetted-chain integral equations using the method of Ng.<sup>6</sup> This method has been shown to be quite accurate when compared to the results of machine simulations and provides a ready method of interpolating for  $S(\Gamma, k)$  as a function of  $\Gamma$ . The integral for  $E_{BS}(\Gamma^0)$  was evaluated numerically and  $\Gamma^0$  was varied to obtain a minimum variational upper bound. Note that the variational parameter in the case of the OCP reference system is really the *charge* of the ion since the system is varied at fixed temperature and volume.

### III. NUMERICAL RESULTS FOR MODELS OF LIQUID Na AND Al

We have obtained minimum variational upper bounds to the structure-dependent excess free energy  $F_s$  using both OCP and HS reference systems for model liquid Na and Al near freezing, using the formalism of the preceding section. The Lindhard dielectric function with and without the exchange-correlation correction of Hubbard, Geldart, and Vosko<sup>13</sup> was used and the results are shown in Figs. 1–7.

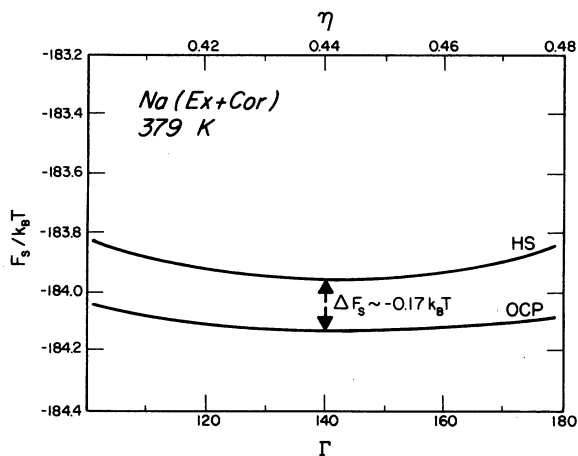


FIG. 1. Comparison of the variational upper bounds to the excess structural-dependent free energy for liquid Na at 379 K, as obtained by using hard-sphere and one-component-plasma reference systems. Here  $r_c = 0.89 \text{ \AA}$ ,  $r_s = 2.14 \text{ \AA}$ , and the exchange-correlation corrections of Hubbard, Geldart, and Vosko (Ref. 13) were used for the dielectric function.

The results for the free energy of liquid Na indicate that the OCP reference system gives a lower bound by  $-0.17k_B T$  and  $-0.4k_B T$  per ion with and without the exchange-correlation correction, respectively (see Figs. 1 and 2). These results indicate that the model ion-ion potential for Na is effectively much *softer* than those of the inert-gas liquids and hence the OCP is a better reference system. This is further supported by fitting experi-

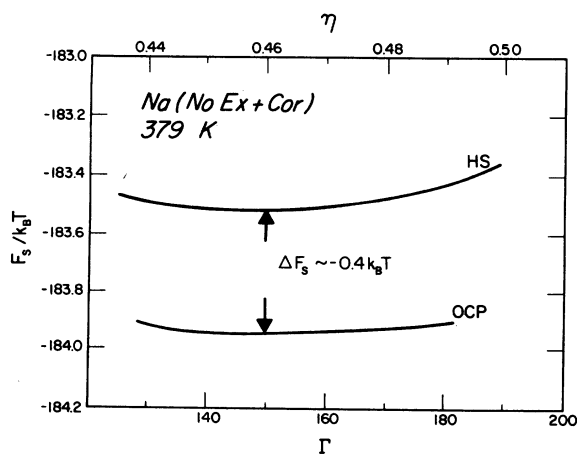


FIG. 2. Same as Fig. 1 except that no exchange-correlation corrections were included in the dielectric function.

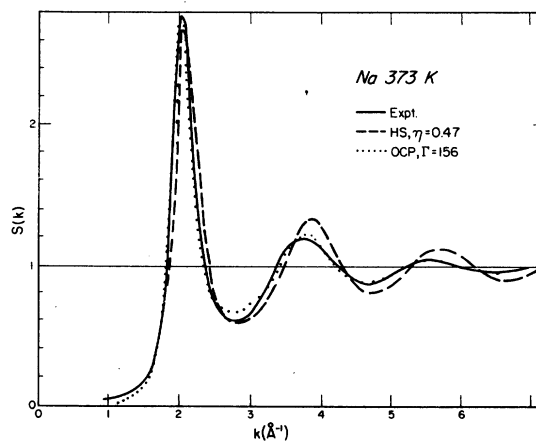


FIG. 3. Comparison of fits to the experimental (Ref. 16) structure factor for liquid sodium at 373 K with HS (hard-sphere) and OCP (one-component plasma) systems.

mental structure factors<sup>16</sup> with both HS and OCP structure factors, as shown in Fig. 3. As is evident, the OCP provides a better overall fit, especially for the higher  $k$  region (see Figs. 3 and 4). The higher  $k$  region reflects the correlations at small ion-ion separations. A better fit<sup>6</sup> has already been demonstrated using  $(1/r^4)$  fluid structure factor from simulations.<sup>17</sup> However, it is important to note that the small  $k$  region (large separations), which reflects the dielectric screening effects, is modeled rather poorly by the OCP system. This, however, does not strongly affect the structure-dependent part of the free energy for the liquid state which lacks long-range order, and the OCP is still slightly better as a reference system in this

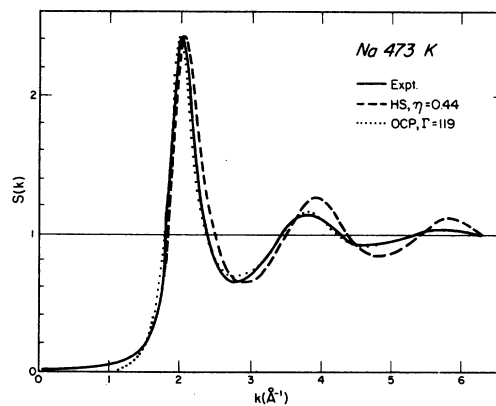


FIG. 4. Same as Fig. 3 except at 473 K.

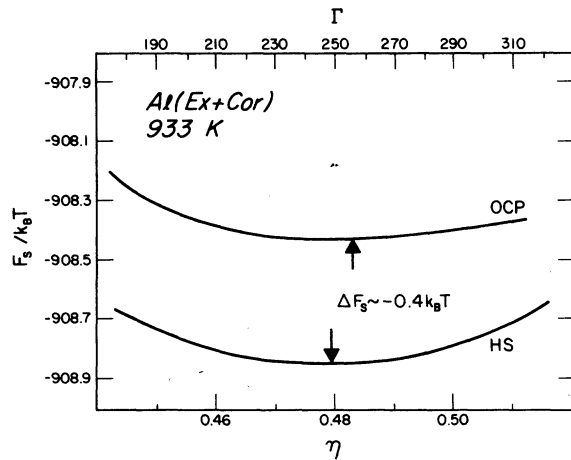


FIG. 5. Comparison of the variational upper bounds to the excess structural-dependent free energy for liquid Al at 933 K using HS and OCP reference systems. Here  $r_c = 0.591 \text{ \AA}$ ,  $r_s = 1.144 \text{ \AA}$ , and exchange-correlation corrections of Hubbard, Geldart, and Vosko were used for the dielectric function.

case. The effective softness of the pair potential here can be attributed to the large empty core radius ( $\geq 1 \text{ \AA}$ ) and low electron density ( $r_s \geq 2 \text{ \AA}$ ) for monovalent alkali metals.

The results for a model liquid aluminum are substantially different. Here the HS reference system provides a better variational bound to the free energy than OCP by  $0.4k_B T$  when exchange-correlation corrections are included (see Figs. 5 and

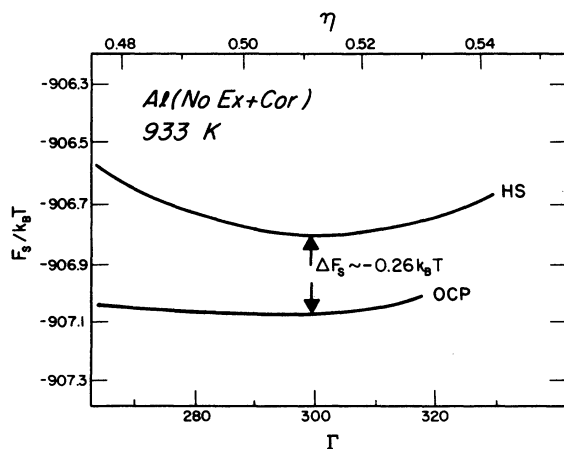


FIG. 6. Same as Fig. 5 except that no exchange-correlation corrections were included in the dielectric function.

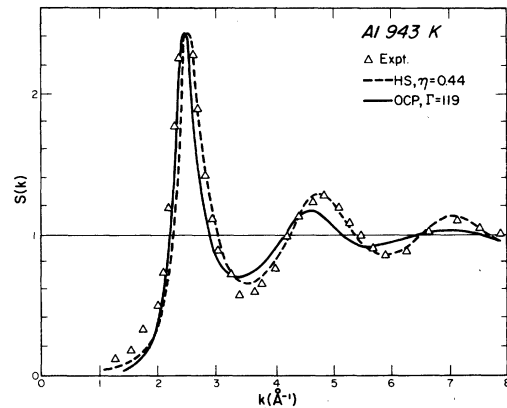


FIG. 7. Comparison of fits to experimental structure factor of Al (quoted in Ref. 18) at 933 K using HS and OCP reference systems.

6). When there is no exchange correlation the OCP is better by  $-0.62k_B T$ . These results can be considered as exhibiting the importance of the exchange-correlation correction in obtaining a realistic model metallic system. Further evidence of the HS reference system is the fact that the HS structure factor provides a rather better fit to the experimental structure factor of liquid aluminum, as shown in Fig. 7.<sup>18</sup> For the model without exchange and correlation the variational bound produced by the OCP is obtained only with very unrealistically large  $\Gamma^0$  ( $\sim 300$ ), much beyond the freezing value ( $155 - 169$ )<sup>5,19</sup> of the OCP system.

We attribute the superiority of the HS for Al to the fact that Al is a polyvalent metal with a small empty core radius ( $r_c \sim \frac{1}{2} \text{ \AA}$ ) and high electron density ( $r_s \sim 1 \text{ \AA}$ ). The dielectric screening is thus much more effective and there are dramatic deviations from the bare Coulomb potential leading to a liquid metal which is better represented as a hard-sphere system than as a one-component plasma.

#### IV. DISCUSSION

By comparing the free energy obtained using both OCP and HS reference systems, we have shown that the OCP can be a better reference system for model alkali metals. The HS system, however, remains the preferred reference system for the polyvalent metals. The difference can be traced to the large variations in  $r_c$  and  $r_s$ , and the density dependence of the dielectric screening. Although our free-energy results are obtained for model sys-

tems using a simple one-parameter pseudopotential and approximate electron dielectric function, the structural consequences which follow from the good fit to the experimental structure factor establish the OCP as a useful and convenient reference system for liquid metals.

An interesting perspective on the variational approach can be obtained by interchanging the roles of "reference" and "real" system in the Gibbs-Bogolyubov inequality [Eq. (5)].<sup>1,14</sup> This procedure yields a *lower* bound to the free energy:

$$NF^0 \leq NF + \langle \Phi^0 - \Phi \rangle_{\Phi} \quad (13)$$

or

$$NF \geq NF^0 + \langle \Phi - \Phi^0 \rangle_{\Phi}, \quad (13')$$

where the potential difference is to be averaged over the distribution functions of the real system associated with the full Hamiltonian  $\mathcal{H}$ . This bound is not very useful for the HS reference potential  $\Phi^0 = \Phi^{\text{HS}}$  on account of the singular nature of the pair interaction, but it gives nontrivial information for the OCP reference system. If the *actual* structure factor were actually identical to the OCP structure factor *over all  $k$  values*, the upper and lower bounds in this case would be identical. The fact that this agreement is very good over a large

range of  $k$  for Na, suggests that not only does the OCP give a lower variational bound to  $F$  than does the HS, but also that the true  $F$  is very well approximated by this variational bound, probably to within a fraction of  $k_B T$ . This result helps explain why the melting properties of the alkalis are very similar to those of the one-component plasma, as discussed by Stishov.<sup>20</sup>

To summarize, the results presented here provide further evidence that the OCP reference system is a useful addition to the repertoire of techniques for studying liquid metals, especially those with soft cores such as the alkalis. The possible advantages of the OCP analog for mixtures (two-component plasma or molten salt) can now be explored for alloys where important problems remain to be solved. We have also shown that the hard-sphere variational method remains the most accurate technique for certain metals, especially polyvalent metals.

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