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Use of the charged-hard-sphere reference system in variational thermodynamic calculations

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We draw attention to a new reference system. This is a system of charged hard spheres embedded in a rigid, uniform, and neutralizing background. The model is attractive since analytical expressions such as the free energy, internal energy, structure factor, etc., are available. The usefulness of the model as applied to the variational study of thermodynamic properties of liquid alkali metals is explored. This model is then compared with similar thermodynamic calculations using separately the neutral hard spheres and the classical one-component plasma as reference systems. Results from this comparison show that the charged-hard-sphere system may be preferred as a reference liquid over the neutral-hard-sphere system or, from the economical and computational viewpoint, over the one-component-plasma system.

I. INTRODUCTION

Much effort[1-5] has been devoted to the study of thermodynamic properties of liquid metals. Because of their simple electronic structures, the liquid alkali metals have often been chosen as prototype elements for research. The thermodynamics of rigid alkali metals has been examined recently[1-10] with use of the variational perturbation techniques. In this approach,[11] one starts with a well-known inequality, namely the Gibbs-Bogoliubov inequality. In very simple terms, this inequality states that the true Helmholtz free energy of a system is bounded above by a chosen reference Helmholtz free energy plus the difference in potential energies between the actual and the reference systems, the latter being averaged over the distribution of the reference liquid. Thus it is clear that the whole variational thermodynamic calculation of liquid metals hinges on the choice of a reference liquid.

A system of neutral hard spheres (NHS) in the Percus-Yevick[1-6] (PY) approximation has been employed widely as a reference liquid. Availability of analytical expressions for all thermodynamic quantities serves to improve numerical accuracy and to facilitate computations, and is one of the main reasons for its popularity. In addition it was discovered[12] that the essential features of the structure in liquid metals is characterized mainly by the repulsive part of the interparticle potential. Naturally the NHS system provides quite a good starting point. Attempts[1-7] to apply the NHS as a reference system in the thermodynamic variational calculation have led to a general conclusion that the NHS model is just as good a reference liquid when applied to liquid polyvalent metals such as Al, Mg, etc., as it was originally tested against Monte Carlo (MC) or molecular-dynamics (MD) computer "experiments" for systems of insulating liquids such as argon. The main reason for its success is found to be intimately related to the stiffer nature of the repulsive part of the pair potentials of polyvalent metals.[1-5] Thus it is no surprise that when applied to liquid alkali metals, the model was found[2] to be a less appropriate reference system. This realization of the inadequacy of the NHS system to simulate liquid alkali metals has spurred further attempts to find an alternative candidate which would duly consider the characteristic softness of the potentials of liquid alkali metals.

The classical one-component plasma (OCP) naturally emerges as the next model for investigation. One obvious advantage of using OCP is, of course, that this system has a soft interparticle potential and thus at least the pertaining soft-potential property of the liquid alkali metals can be incorporated. The works of Evans and Sluckin,[8] Mon *et al.*,[9] Iwamatzu *et al.*,[12] and others[10,14-16] represent some very recent efforts to explore the usefulness of this model as applied to metals. While the results of these studies point to the fact that the OCP is generally superior (in the sense of predicting lower free energy) over a system of NHS, progress in exploiting the OCP as a useful reference in the study of thermodynamics of simple metals has been slow. The reason is that in order to carry out an accurate thermodynamic calculation it is highly desirable to *a priori* obtain reliable MC or MD computer-simulation results. But highly reliable simulation can only be achieved at the expense of enormous computing time. Moreover, although presently available simulation results for the thermodynamic quantities have been fitted to empirical formulas, there is as yet ambiguity regarding the reliability of the formulas proposed. Such implications can be seen from the most recent work of Slattery *et al.*[17] who raised the question about the number-of-particle dependence in the simulation process. One consequence is that for each newly available simulation result, strictly speaking, one has to repeat the whole calculation, a procedure which is time consuming and cumbersome.

In this paper we draw attention to another promising reference system which not only retains many of the attractive features of the NHS system discussed above, but is also capable of taking proper account of the less repulsive nature of the pair potentials. This is the model of charged hard spheres (CHS). As a prerequisite to thermodynamic variational studies, one needs to know the thermodynamics (such as the Helmholtz free energy, the radial distribution function, etc.) of this system. In the mean spherical approximation, such a system has been solved exactly by Palmer and Weeks.[18] These authors derived analytical expressions for the structural and thermodynamic quantities which can be used in the variational treatment. Just as the NHS model has been tested against exact MC or MD computer simulations, the CHS model has also been examined[19–23] very recently against machine calculations. Remarkably good agreement is found, as compared with MC simulation works of an OCP system.[23] Already the CHS model has been adopted by Blum and Narten,[24] Singh and Holz,[25] and Chaturvedi *et al.*[26] to understand the liquid structure factors of alkali metals. The theoretical results obtained are encouraging.

In the following we choose the CHS model as our reference system. Conceptually this model is essentially similar to the classical OCP (for review, see Baus and Hansen[27] and also Ichimaru[28]) except that in the CHS model we attach a hard-sphere (HS) radius to the point charge so that penetration of other "plasma" particles is strictly prohibited. It should be recognized that the introduction of a HS diameter as a distance of closest approach is not a theoretical artifact but is based on realistic physical ground; the situation can be considered to correspond to the operation of a strong Coulomb repulsive force that comes into effect when the ions are coming too close to each other.[25,29] In principle, therefore, we have two free parameters, the HS diameter and the plasma parameter (defined to be the ratio of the electrostatic energy to thermal energy of a particle), to be determined for a complete specification of the CHS system. However, as a reasonable approximation, we choose the variational parameter to be the HS diameter. Some justification for this choice can be drawn from the works of Minoo *et al.*,[30] Hansen,[31] and Singh and Holz.[25] While keeping the plasma parameter constant, our calculation appears to yield a better description for the calculated thermodynamic properties. This conclusion can be inferred from current thermodynamic results[2,4] obtained from the same variational approach but using the NHS as a reference. Generally, the latter has been found to be not very realistic in simulating a reliable liquid structure factor [denoted herein by $S(q)$] appropriate for the liquid alkali metals and hence the accuracies of the computed Madelung and band structure energies are themselves in doubt. We shall find in this work that the calculated Helmholtz free energy for the CHS model is slightly higher than that determined using a NHS system. From the variational viewpoint, this seems to suggest that the NHS system is a better reference liquid. As it turns out, this result for the NHS system is only fortuitous resulting from the cancellation of errors in the inaccurate terms. We shall present numerical results and show that such a discrepancy may be attributed to (i) an inconsistent use of the radial distribution function and (ii) a less-accurate description of $S(q)$ for the alkali metals within the HS theory. Further, from its physical resemblance to OCP, when the $S(q)$ obtained for both CHS and OCP reference liquids are compared, we find that they agree very well with each other and with experiments. We conclude this paper by examining the effects of exchange-correlation corrections on the free energies calculated using the three reference systems considered here.

II. CHARGED-HARD-SPHERE MODEL

In the mean spherical approximation, a system of CHS interacting through a pairwise, central potential

$$V(r)=\begin{cases}\infty, & r<\sigma\\ \dfrac{Z^2e^2}{r}, & r>\sigma\end{cases} \tag{1}$$

where Z and σ are, respectively, the nominal valence and HS diameter, has been exactly solved by Palmer and Weeks.[18] Singh and Holz,[25] in their studies of the liquid structure factors of alkali metals, have carried out a Fourier transform of the direct correlation function derived by Palmer and Weeks. We shall make use of this analytical $S(q)$ in the following; the interested reader should refer to their original papers for mathematical details.

This system of CHS is now our reference system for the variational calculation. In the present work, we use the Gibbs-Bogoliubov inequality[32,33] which states that if we have a Hamiltonian H for which the Helmholtz free energy is F (the actual system), and if we have a reference system at the same density and temperature as the actual system where H_{ref} and F_{ref}, are, respectively, its Hamiltonian and Helmholtz free energy, then

$$F\le F_{\text{ref}}+\langle H-H_{\text{ref}}\rangle_{\text{ref}}\,. \tag{2}$$

The $\langle\cdots\rangle_{\text{ref}}$ in Eq. (2) means an ensemble average over all the configurations of the chosen reference system. It is clear from Eq. (2) that if the reference system mimics very closely the actual system, then the perturbation term would be small.[16] On the other hand, if F_{ref} does not characterize the true system very well, one would anticipate a large perturbation and the free energy obtained will poorly approximate the correct value.

Having stated the variational method, we proceed to calculate the model Helmholtz free energy. The reference Helmholtz free energy can be obtained from the work of Palmer and and Weeks.[18] This is done by noting that the excess internal energy given by them is integrable immediately, giving[22,34]

$$\begin{aligned}F_{\text{ref}}^{\text{ex}}=&\frac{4\eta-3\eta^2}{(1-\eta)^2}k_BT\\&-\frac{Z^2}{\sigma}\Bigg\{1+\eta-\frac{\eta^2}{5}+\frac{2}{\kappa}(1+2\eta)\\&\qquad-\frac{2}{3}\frac{(1+2\eta)^3}{(1-\eta)^3}\frac{1}{\kappa^2}\\&\qquad\times\left[\left[1+\frac{2(1-\eta)^3\kappa}{(1+2\eta)^2}\right]^{3/2}-1\right]\Bigg\}\,,\end{aligned} \tag{3}$$

where η is the packing fraction, k_B is the Boltzmann constant, T is the temperature, and $\kappa=(12\eta^{2/3}\Gamma)^{1/2}$ in which Γ is the conventional plasma parameter. In deriving this formula use is made of the fact that the case $\kappa=0$ corresponds to a system of NHS.[35] We have three possibilities[22] at hand depending on the equation of state used. Here we choose the Carnahan-Starling equation of state[36] for the system of NHS because it has been checked[37] in the literature to reproduce the MC results extremely well.

As for the perturbation term in Eq. (2), we have formulated our theory using the energy-independent nonlocal model pseudopotential.[38] Because of the nonlocal nature of the pseudopotential, the perturbation term looks somewhat different as compared with those using local potential.[1] Operating straightforwardly we have

$$\langle H - H_{\mathrm{ref}} \rangle_{\mathrm{ref}}^{\mathrm{ex}} = \frac{\rho_d^2}{\sigma} \left\{ 1 + \eta - \frac{\eta^2}{5} + \frac{1+2\eta}{\kappa} \left[1 - \left[1 + \frac{2(1-\eta)^3 \kappa}{(1+2\eta)^2} \right]^{1/2} \right] \right\} - \frac{Z_{\mathrm{eff}}^2}{\pi} \int_0^\infty dq\, S_{\mathrm{CHS}}(q) G_N^{\mathrm{EC}}(q) \; . \qquad (4)$$

Here ρ_d is the depletion charge which vanishes in local pseudopotential theory, $Z_{\mathrm{eff}}^2 = Z^2 - \rho_d^2$ is the effective charge,[38] $S_{\mathrm{CHS}}(q)$ is the structure factor given by Eq. (5) in the work of Singh and Holz[25] and $G_N^{\mathrm{EC}}(q)$ is the normalized energy wave-number characteristic with exchange-correlation corrections included.[38] When compared with the usual OCP model derived from Monte Carlo simulation,[9,10] the first term in Eq. (4) is just the deviation of the Madelung energy from its value in the reference system. It can be written in this form because the variational parameter is now chosen to be the HS diameter. The second term in Eq. (4) is the band structure energy. It is interesting to note that when $\Gamma \to 0$ (corresponding to $\kappa \to 0$) Eqs. (3) and (4) reduce exactly to the familiar NHS result.[6]

Although, for the purpose of comparison, we also calculate the thermodynamic properties of alkali metals using NHS and OCP as reference systems, we will not write down the mathematical expressions here. For the NHS we refer the reader to the work of Lai *et al.*[6] and for the OCP to the work of Iwamatzu *et al.*[13]

The variational thermodynamic calculation can now be done by varying the HS diameter appearing in the sum of Eqs. (3) and (4). To carry out OCP calculations, the liquid structure factors $S_{\mathrm{OCP}}(\Gamma, q)$ are needed. For these we use the readily accessible table of Rogers *et al.*[39] All computations were done at or near the freezing point of all alkali metals. [Li was excluded in the OCP calculation as the minimum value of Γ lies outside the maximum Γ ($\Gamma_{\max} = 180$) available to us. Moreover, this $\Gamma_{\max}$ value also corresponds to the Γ at which the OCP system freezes to a solid phase.[17,40]]

III. RESULTS AND DISCUSSION

We present in Table I our theoretical calculations of the excess Helmholtz free energies. Scrutinizing the entries carefully, the following two points are observed.

(a) The Helmholtz free energy using the OCP as a reference system has the lowest value for any EC correction.

(b) The NHS reference system has a Helmholtz free energy lower than that of the CHS but higher as compared with the OCP. This is true for all of the EC corrections considered.

The first point noted above is consistent with that found by Mon *et al.*[9] applying a local pseudopotential theory to the case of liquid Na. There is, however, one minor difference. The present calculation which adopts a full nonlocal pseudopotential appears to yield a slightly better $S(q)$ ($\eta = 0.456$ for Na) relative to that obtained by Mon *et al.*[9] ($\eta \simeq 0.44$, to compare well with experiment the value of η should be 0.47). At this point it is perhaps appropriate to mention a similar work by Ross *et al.*[10] These authors have also carried out a similar variational calculation for liquid lithium at various temperatures. However, the model potential used in their work is too crude to validate the conclusion that the OCP is a good reference fluid. For example, we note that at the minimum of F, they obtained a plasma parameter, at the melting point, equal to 130.5. This Γ is significantly different from the one predicted by Iwamatzu *et al.*[13] ($\Gamma > 180$) using the same nonlocal pseudopotential theory as used in this work. Point (b) is unexpected because the proposed CHS model, as already mentioned in the Introduction, was claimed to be physically closer to the actual system as compared with the NHS model. But then why

TABLE I. Excess Helmholtz free energies F^{ex} for liquid alkali metals. EC refers to exchange-correlation correction (see text). SI, Singwi *et al.* (Ref. 50); VS, Vashishta-Singwi (Ref. 51); TW, Toigo-Woodruff (Ref. 52). Calculations were done at the melting points of each metals. All in atomic units.

EC	Model	Na	K	Rb	Cs
SI	NHS	−0.209 11	−0.156 64	−0.138 97	−0.117 54
	CHS	−0.208 91	−0.156 50	−0.138 78	−0.117 45
	OCP	−0.209 64	−0.157 13	−0.139 39	−0.118 01
VS	NHS	−0.209 03	−0.155 79	−0.137 75	−0.115 49
	CHS	−0.208 74	−0.155 47	−0.137 30	−0.115 10
	OCP	−0.209 49	−0.156 12	−0.137 95	−0.115 70
TW	NHS	−0.209 44	−0.156 96	−0.139 27	−0.117 60
	CHS	−0.209 16	−0.156 65	−0.138 85	−0.117 24
	OCP	−0.209 90	−0.157 28	−0.139 47	−0.117 80

is it that the excess F is lower for the NHS system? Upon analyzing the theory we find two possible sources of errors. In the first place, the discrepancy may lie in the reference liquid structure factor. For a system of NHS, the HS potential tends to be too repulsive for the alkali metals where the potentials are known to be considerably softer.[2,41] This less-accurate representation of the liquid structure factor would yield unreliable values in the calculation of Madelung and band structure terms. Once this happens, the $F_{\mathrm{ref}}^{\mathrm{ex}}$ given in Eq. (2) will deviate more from the true F and the second perturbation term is hence larger. This further implies that due care must be exercised when comparing F between various reference systems. Second, the use of the PY approximation for a HS system introduces an additional uncertainty. This is because the PYHS theory has been examined[42–44] to be accurate only for low-density fluids (typically $\eta < 0.3$) and hence the free energy obtained using PYHS structure factor cannot be identified as the true upper bound to the F of alkali metals. It could be that if an "exact" HS structure factor (or radial distribution function) were used, the resulting F might not be lower than the CHS model. In order to support or refute our arguments we have repeated the above calculations using the method of Edwards and Jarzynski[45] (see also Ref. 2). For the radial distribution function of a HS system, we have adopted (i) for the PY theory, the numerical table of Throop and Bearman[42] and (ii) for the exact theory the one due to Verlet and Weis[43] (VW). The results are displayed in Table II. It is interesting to note from the table that for all of the alkali metals considered the structure-dependent terms [Eq. (3.4) of Ref. 45] calculated using an exact radial distribution function have values lying above the corresponding ones done within the PY theory. The difference in the two results is of the order of $\sim 10^{-4}$ a.u., a value which, though small, is not entirely negligible when comparing the F values between the NHS and CHS models. Incidentally, the above findings for the Helmholtz free energies calculated using PY and VW radial distribution functions have also been obtained by Bratkovosky *et al.*[7] for liquid Na (see Table II).

For more relevant evidence to further test our conjecture, we depict the reference liquid structure factors for Na, K, Rb, and Cs calculated using both the NHS and CHS reference systems. The values of η given in these figures are those corresponding to the minima of each F. For the purpose of judging the reliability of our computed $S(q)$, we compared the $S(q)$ obtained from these two models with the most recent experimental data.[46–48] The results are given in Figs. 1–4. Analyzing all these figures we see that the $S(q)$ obtained in the context of the CHS model agree very well with experiments (notably at and near the first peak) relative to the NHS system. For comparison, we present also the reference liquid structure factor calculated using the OCP model. Note that the theoretical Γ values for the Na, K, Rb, and Cs, corresponding to the minima of each F, are, respectively, 131.45, 134.52, 127.00, and 127.58. The structure factors at these values are unfortunately not readily available. Instead we have plotted the $S_{\mathrm{OCP}}(\Gamma,q)$ using the nearest Γ value, i.e., $\Gamma = 130$, in each case. Before commenting on the results, we first recall the computed F_{OCP} listed in Table I. It is seen that the F_{OCP} values for all of the alkali metals have free energies lower than the ones given by the NHS model. These results indicate that to study the thermodynamic properties of those metals for which the repulsive cores are comparatively soft (relative, for example, to liquid argon), the OCP is a good reference liquid.[49] In view of the fact that both OCP and CHS models have interparticle potentials of the Coulombic type (except for a hard-core insertion for the latter) both $F_{\mathrm{ref}}^{\mathrm{ex}}$'s should

TABLE II. Contributions of structural terms [Eq. (3.4) of Ref. 45] of all liquid alkali metals. PY and VW stand, respectively, for Percus-Yevick and Verlet-Weis (see text). Singwi *et al.* (Ref. 50) exchange-correlation correction was used. Theoretical results for the total Helmholtz free energies of Bratkovsky *et al.* are taken from Ref. 7 (last two rows). All in atomic units.

	Na	K	Rb	Cs
PY (10^{-3} a.u.)	−0.3930	0.1459	0.2646	0.9330
VW (10^{-3} a.u.)	−0.2888	0.2077	0.3207	0.9875
PY (a.u.)	−0.236 36			
VW (a.u.)	−0.236 16			

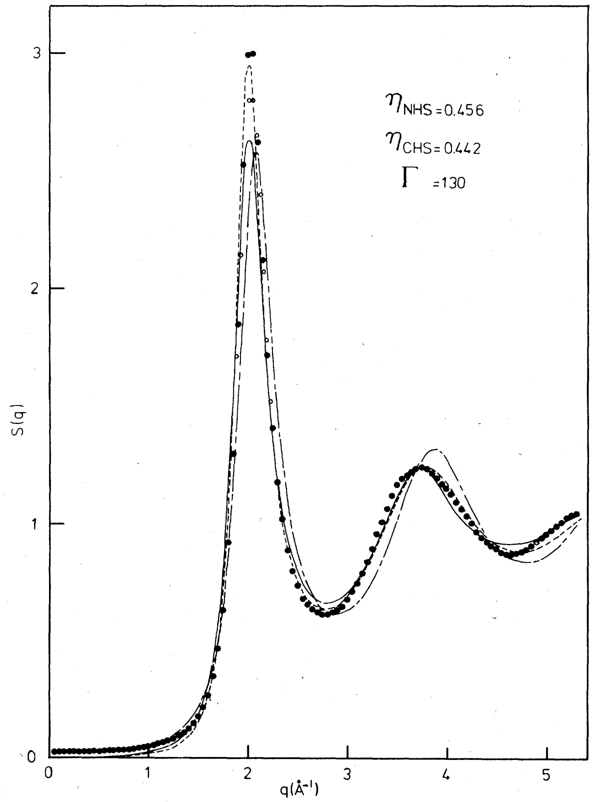

FIG. 1. Liquid structure factor for Na calculated at $T = 100\,^{\circ}\mathrm{C}$ using three reference systems. Notations are — — — for CHS, – - – for NHS, and —— for OCP. Experimental results, denoted by solid circles, are provided by van der Lugt (Ref. 48), and open circles are taken from Greenfield *et al.* (Ref. 46).

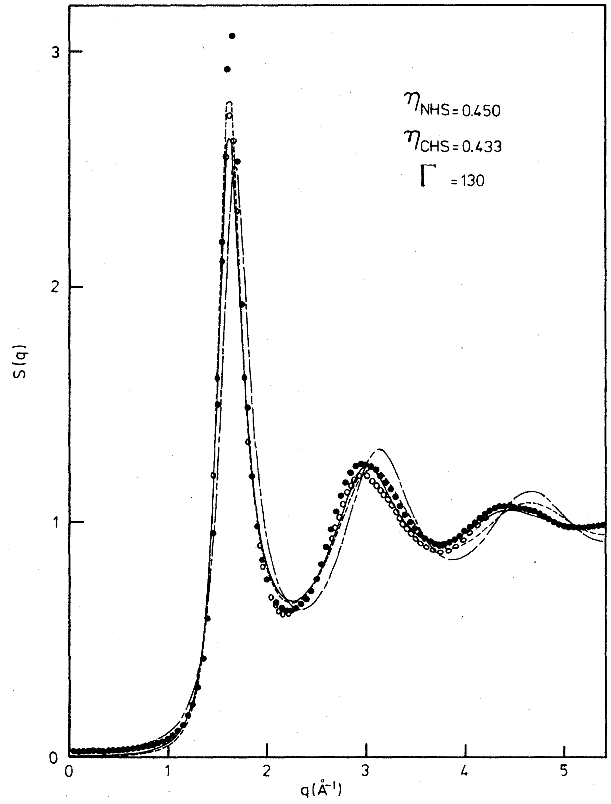

FIG. 2. Liquid structure factor for K calculated at $T = 63.5\,^\circ\mathrm{C}$ using three reference systems. See Fig. 1 for notation.

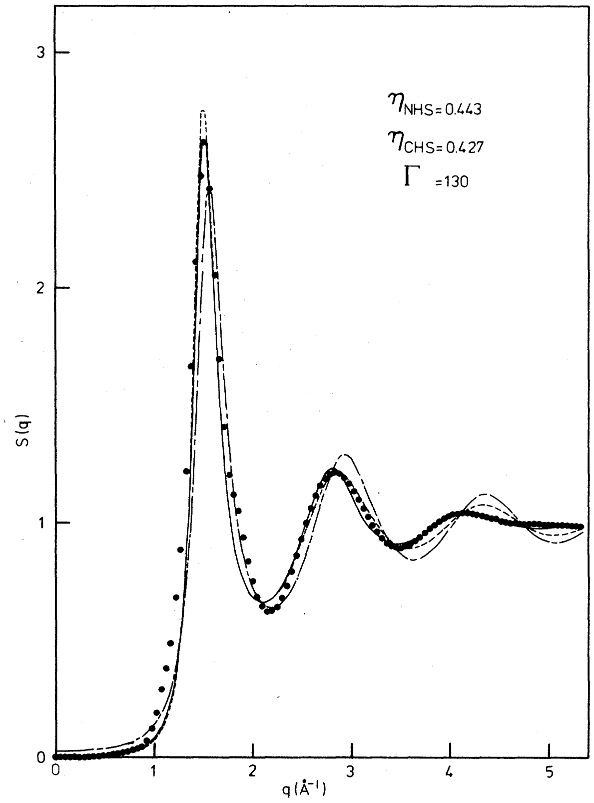

FIG. 3. Liquid structure factor for Rb calculated at $T = 38.9\,^\circ\mathrm{C}$ using three reference systems. See Fig. 1 for notation. Here the experimental results, denoted by solid circles, are taken from Zei (Ref. 47).

mimic well the true F of alkali metals. Indeed, examination of the reference structure factors of all alkali metals obtained via OCP and CHS (see Figs. 1—4) shows striking agreement between the two. (In detail, the OCP model appears to agree slightly better in all the alkali metals, especially for the higher-q regions. That explains why the OCP system yields a lower Helmholtz free energy.) The corresponding results for the NHS model, on the other hand, deviate significantly from the OCP and CHS and from experiments.

To explore further we give in Table III the values of the HS diameters obtained in the CHS and NHS models for all of the alkali metals. Systematically we observe that the σ's for the CHS are smaller than those determined in the NHS model. This result is encouraging because a smaller σ value means a better and closer description in the physical situation of the repulsive cores of the alkali metals (for metals with softer pair potential, the ions should be able to come a bit closer before the strong Coulombic repulsion comes into play and prevents the ions approaching any closer). In this context we find that the CHS system not only retains many of the desirable features of a NHS system but, most importantly, accounts for the characteristic softness of the interparticle potential.

We now turn to the discussion of the effects of EC correction on the three reference systems used (see Table

TABLE III. Hard-sphere diameters σ determined variationally using NHS and CHS systems. EC refers to exchange-correlation correction (see text). SI, Singwi *et al.* (Ref. 50); VS, Vashishta-Singwi (Ref. 51); TW, Toigo-Woodruff (Ref. 52). All in atomic units.

EC	Model	Na	K	Rb	Cs
SI	NHS	6.2331	7.6877	8.2102	8.8560
	CHS	6.1678	7.5859	8.1106	8.7095
VS	NHS	6.2062	7.6038	8.0695	8.6637
	CHS	6.1621	6.5621	8.0683	8.6444
TW	NHS	6.2133	7.6422	8.1338	8.7724
	CHS	6.1712	7.6084	8.1377	8.7661

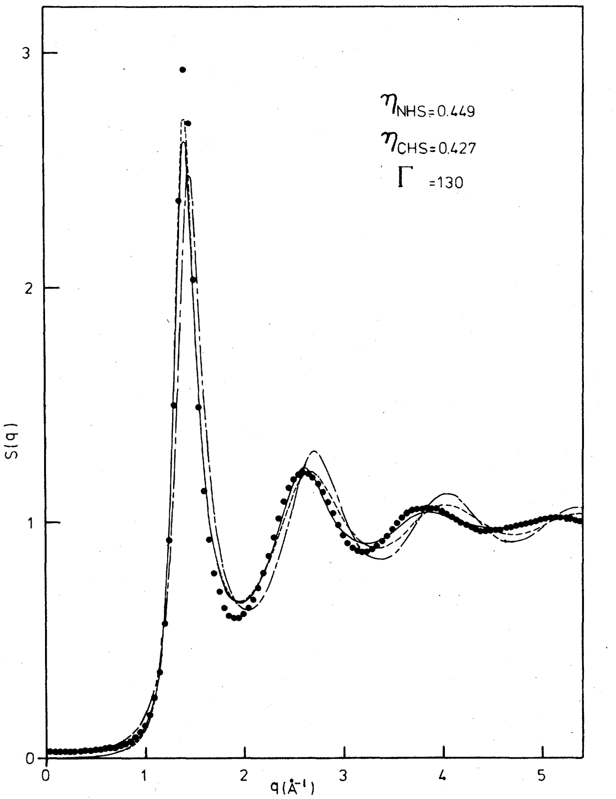

FIG. 4. Liquid structure factor for Cs calculated at $T=28.6\,^{\circ}\mathrm{C}$ using three reference systems. See Fig. 1 for notation.

I). We consider three commonly used EC functions, i.e., those of Singwi *et al.* (denoted by SI in the present work),[50] Vashishta and Singwi (VS),[51] and Toigo and Woodruff (TW).[52] Our calculated results show that the Helmholtz free energies using TW EC corrections have the lowest free energy, though, for the three reference systems corresponding to the same TW or in fact for any EC function considered here, the relation $|F_{\mathrm{OCP}}^{\mathrm{ex}}| > |F_{\mathrm{NHS}}^{\mathrm{ex}}| > |F_{\mathrm{CHS}}^{\mathrm{ex}}|$ remains unchanged. There are two points deserving attention. First, this result substantiates the work of Mon *et al.*[9] who applied a local pseudopotential theory along with the EC corrections of Hubbard[53] and Geldart and Vosko[54] to the case of sodium. They found that with the inclusion of EC corrections, the OCP leads to lower F relative to the NHS model. The present work quantitatively justifies their calculation and shows that this is true for all the alkali metals (except Li). The second point to be noted is that the present calculations provide evidence that the fact that the free energy $F_{\mathrm{CHS}}^{\mathrm{ex}}$ is found to be higher than the $F_{\mathrm{NHS}}^{\mathrm{ex}}$ is not due to the use of different EC functions.

IV. CONCLUSION

It is proposed in the present work that a system of charged hard spheres may be a useful reference liquid in the thermodynamic variational calculation for those metals where the pair potentials are known to be soft (compared, for example, to the liquid argon). Although the OCP computer-simulation experiment remains the best reference system (in the sense of yielding lowest free energy), it has the practical disadvantage of not being analytically available, in addition to requiring a large amount of computing time for an effective implementation. In this respect the CHS model may be a good reference liquid to use; this model, besides being analytically solvable, has all the advantages that a neutral-hard-sphere system has.

Analysis of the calculated free energies has led to a conclusion that the Percus-Yevick hard-sphere theory is not accurate enough for yielding a reliable free energy. Both the OCP and the CHS reference liquids characterize very well the liquid structure factors of all alkali metals (relative, of course, to the NHS model) and compare favorably with most recent experiments. On the other hand, the NHS system, though fortuitously having lower free energy values (through cancellations of inaccurate terms in integrations) than the CHS system, does not simulate the structures of liquid alkali metals very well and hence its use for quantitative studies requires further investigation.

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[11] Here we are only concerned with one of the many variational perturbation methods to be described below. Because of its widespread use in recent developments of liquid state theory

to metals, we believe that such an emphasis is beneficial. For full details of other variational approaches the readers are referred to the excellent review article by Barker and Henderson, Ref. 37.

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