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Thermodynamics and structure of liquid alkali metals from the charged-hard-sphere reference fluid

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The evaluation of thermodynamic properties of liquid alkali metals is reexamined in the approach based on the Gibbs-Bogoliubov inequality and using the fluid of charged hard spheres in the mean-spherical approximation as reference system, with a view to achieving consistency with the liquid structure factor. The perturbative variational calculation of the Helmholtz free energy is based on an *ab initio* and highly reliable nonlocal pseudopotential. Only limited improvement is found in the calculated thermodynamic functions, even when full advantage is taken of the two variational parameters inherent in this approach. The role of thermodynamic self-consistency between the equations of state of the reference fluid derived from the routes of the internal energy and of the virial theorem is then discussed, using previous results by Høye and Stell [J. Chem. Phys. **67**, 439 (1977)]. An approximate evaluation of the corresponding contribution to the free energy of liquid alkali metals yields appreciable improvement in both the thermodynamic functions and the liquid structure factor. It thus appears that an accurate treatment of thermodynamic self-consistency in the charged-hard-sphere system may help to resolve some of the difficulties that are commonly met in the evaluation of thermodynamic and structural properties of liquid metals.

I. INTRODUCTION

In the last fifteen years there has been great progress in our theoretical understanding of the thermodynamic properties of liquid metals. A widely used technique is the variational approach based on the Gibbs-Bogoliubov inequality. This inequality can be stated as follows. Let the liquid metal, at given temperature and density, be described by the Hamiltonian H_{true}, which determines the Helmholtz free energy F_{true} by

$$\exp(-\beta F_{\text{true}})=\text{Tr}[\exp(-\beta H_{\text{true}})] , \tag{1}$$

with $\beta=1/k_BT$. If one chooses a reference system in the same thermodynamic conditions, with Hamiltonian H_{ref} and Helmholtz free energy F_{ref}, the Gibbs-Bogoliubov inequality then puts an upper bound on F_{true} as[1]

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

The brackets $\langle\ \rangle_{\text{ref}}$ in Eq. (2) denote a statistical ensemble average over all the ionic configurations of the reference system.

It is clear from Eq. (2) that the inequality can be used to advantage if a judicious choice is made of the reference system. Two general criteria need to be fulfilled. First, the reference system should mimic well enough, at a primitive level, basic features of the real system such as the liquid structure and the interparticle interaction. The second criterion has to do with practical aspects, that is, all the thermodynamic quantities of the reference system should be readily available, preferably in analytical form or at least in a form that can be conveniently used. Among several possible choices that are available in the literature, the neutral-hard-sphere system,[2-6] the one-component classical plasma,[7-19] the charged-hard-sphere system[15,20-23] and the soft-sphere (inverse power potential) system[17,24-26] have been considered as appropriate reference systems for liquid metals.

The system of neutral hard spheres (NHS) was first investigated because its liquid structure is in qualitative accord with experiment for many liquid metals[27] and its structural and thermodynamic functions are known in closed analytical form (see, for example, Ref. 6). However, the NHS system is not as successful as would be expected. It can only provide a qualitative description for the thermodynamic properties of liquid metals. For example, it has been found[17] that attempts to quantitatively evaluate the pressure of a liquid metal by a pseudopotential variational approach would often lead to unrealistic results. Furthermore, for some liquid metals such as the alkalis the NHS liquid structure factor fails to describe correctly the actual interionic correlations. Such failures are now understood and can quite generaly be attributed to the NHS potential being too "hard" for real metals.[28]

These defects of the NHS reference system quite naturally led to investigations of the usefulness of the one-component classical plasma (OCP), consisting of point particles carrying a charge Ze and embedded in a homogeneous neutralizing background. The OCP model has been extensively studied both theoretically[29-34] and by computer simulation[35-38] as a function of the plasma parameter Γ, defined as the ratio of the electrostatic energy Z^2e^2/R_s to the thermal energy k_BT with R_s the ion sphere radius (see also the reviews by Baus and Hansen[39] and by Ichimaru[40]). Reliable data on its structural and thermodynamic properties are thus readily available. In addition, the OCP structure factor [hereafter referred to as $S(q,\Gamma)$] reproduces surprisingly well the measured structure factor of real liquid metals.[7,10,15,19] However, the use of the OCP as a reference system in variational studies of liquid metals[7-19] has brought to light a general difficulty. Irrespective of the pseudopotential used in the variational approach, the variationally determined value of the plasma parameter for all the alkali liquid metals is about 130,[10,12,14,15,19] much less than that anticipated from liquid structure data ($\Gamma \approx 170$). Thus, although with $\Gamma \approx 130$ the numerical value of the excess entropy is closer to experiment than that obtained from the NHS, the quality of $S(q,\Gamma)$ would be appreciably deteriorated. The apparent contradiction between excess entropy and liquid structure factor in the OCP approach remains unresolved, although various critical discussions have been offered[12,14,17,19,41] and efforts at understanding this puzzle continue.[19] One can perhaps infer from these studies that the OCP thermodynamic functions may still be inadequate for quantitative thermodynamic calculations on liquid metals. Accordingly, there has been a gradual shift of attention to other reference systems, which are somewhat more complicated than the NHS and OCP. Two closely related and competing models have been considered very recently.

The first is the system of charged hard spheres (CHS). This model differs from OCP in that each charge is enclosed in a hard sphere with radius $\sigma/2$. Accordingly, the CHS model is characterized by two disposable parameters, that is, the charge Ze and the hard-sphere diameter σ. The model has been solved in the mean-spherical approximation by Palmer and Weeks[42] and examined by computer simulation.[43] Much attention has been focused on the possibility of exploiting the CHS in the study of the OCP.[29-31,33,34] Apart from early calculations on liquid structure factors,[44,45] it is only recently that quantitative attempts have been made to examine the usefulness of the CHS in understanding the structure[20,23] and the thermodynamic properties[15,21] of liquid metals.

The second reference system that has recently been made use of is the hard-sphere Yukawa potential model in the mean-spherical approximation. Basically, this approach differs from the CHS approach in that screening of the ions by the conduction electrons is partially included already in the reference system. From the variational viewpoint this approach is more flexible, but the expressions involved in the mean-spherical approximation are considerably more complex. In fact, using different nonlocal pseudopotentials quite different results have been obtained (see the recent work by Li, Moore, and Wang[46] and by Hausleitner and Hafner.[47]).

It can be seen from the above brief survey that there still is a need for more detailed examination of thermodynamic and structural properties of liquid metals. Obviously, with just the NHS and OCP systems it is not very likely that one may proceed much further than our present understanding. For more quantitative work, the trend seems to require moving to somewhat richer reference systems such as the CHS or the hard-sphere Yukawa type. In this paper we adopt the CHS model as our reference system and examine the possibility of quantitatively using it in variational thermodynamic studies. For concreteness we have chosen to focus on liquid alkali metals, although the approach may also be useful for polyvalent liquid metals.[21] As for the pseudopotential, we use the modified generalized nonlocal model pseudopotential (GNMP) of Li, Li, and Wang.[48] In contrast to previous work by one of us,[15] we now have both the packing fraction $\eta = \pi\rho\sigma^3/6$, ρ being the particle number density, and the plasma parameter Γ as variational parameters. For purposes of analysis we compare these results with those of one-parameter variational calculations, in which Γ is taken from theoretical work on liquid structure[19] or evaluated from the ionic valence. This will serve to draw attention to the importance of thermodynamic self-consistency in the variational theory. Making use of earlier results by Høye and Stell[49] we shall discuss, in particular, the relation between thermodynamic self-consistency for the reference system and the variational theory, as well as the possibility of achieving mutually consistent results for the excess entropy and the liquid structure factor.

The layout of the paper is briefly as follows. In Sec. II we summarily give the essential expressions needed in the thermodynamic calculations. Section III is devoted to the presentation of numerical results and their discussion, leading to the discussion of the role of thermodynamic self-consistency in Sec. IV. Finally, Sec. V summarizes our main conclusions.

II. THEORY

In this section we summarize the main expressions needed in the calculation. The system of charged hard spheres consists of particles having charge Ze and diameter σ, embedded in a uniform neutralizing background. The particles interact with each other via the potential

$$V(r)=\begin{cases} \dfrac{(Ze)^2}{r} & (r>\sigma) \\ \infty & (r<\sigma) \, . \end{cases} \tag{3}$$

For this hard-core-type potential treated in the mean-spherical approximation (MSA), Palmer and Weeks[42] derived an analytical solution for the direct correlation function and hence, after Fourier transformation, one can easily obtain the CHS liquid structure factor $S(q,\Gamma,\eta)$ (see Ref. 29 for the detailed expression). The excess internal energy expression enters directly the Palmer-Weeks solution and is given as a function of η and Γ by

$$U_{\mathrm{CHS}}^{\mathrm{ex}}=-k_B T\frac{\Gamma}{2\eta^{1/3}}\left[1+\eta-\frac{1}{5}\eta^2-\frac{1+2\eta}{\kappa}[(1+2\kappa\xi)^{1/2}-1]\right], \tag{4}$$

where $\xi=(1-\eta)^3/(1+2\eta)^2$ and $\kappa=(12\eta^{2/3}\Gamma)^{1/2}$. The two quantities $S(q,\Gamma,\eta)$ and U^{ex} are precisely those needed in Eq. (2). From Eq. (4) it is straightforward to calculate the excess Helmholtz free energy of the CHS by integration with respect to Γ, yielding

$$F_{\mathrm{CHS}}^{\mathrm{ex}}=F_{\mathrm{NHS}}-k_B T\frac{\Gamma}{2\eta^{1/3}}\left[1+\eta-\frac{1}{5}\eta^2+\frac{2(1+2\eta)}{\kappa}-\frac{2(1+2\eta)}{3\xi\kappa^2}[(1+2\kappa\xi)^{3/2}-1]\right]. \tag{5}$$

In the above F_{NHS} is the excess free energy of the NHS, corresponding to the case $\Gamma=0$, over the ideal gas free energy. The expression for this quantity will depend on the form of the equation of state (virial, compressibility, or Carnahan-Starling) that one chooses and these forms are all available in the literature (see MacGowan[30]).

At this point it is appropriate to digress a moment and make a relevant remark. Since the expression (5) for the excess Helmholtz free energy of the CHS is obtained from the internal energy, it is related to the radial distribution function and can be expected to yield the most accurate thermodynamic information. On the other hand, from the statistical-mechanical viewpoint, one may also determine the excess Helmholtz free energy from the virial or the compressibility equations of state. In an exact theory these three alternative methods should yield the same value for the free energy. However, different thermodynamic results are obtained by the above three routes in the MSA. This problem of thermodynamic inconsistency is one of the main defects of the mean-spherical approximation and has been a subject of great theoretical attention.[50] In particular, Høye and Stell[49] made an interesting study of its consequences for the general case of hard-core, orientation-independent potentials. We shall discuss this point further in Sec. IV. We return now to Eq. (5).

By making use of Eqs. (2), (4), and (5) the Helmholtz free energy of a liquid metal is readily evaluated and is given (per ion) by

$$\begin{aligned}F=&F_{\mathrm{id}}+F_{\mathrm{CHS}}^{\mathrm{ex}}+E_{\mathrm{EG}}+F_d-\frac{Z_{\mathrm{eff}}^2}{\pi}\int_0^\infty dq\, S_{\mathrm{CHS}}(q,\Gamma,\eta)G^{\mathrm{EC}}(q)\\&-k_B T\frac{(\Gamma_{\mathrm{eff}}-\Gamma)}{2\eta^{1/3}}\left[1+\eta-\frac{1}{5}\eta^2-\frac{1+2\eta}{\kappa}[(1+2\kappa\xi)^{1/2}-1]\right].\end{aligned} \tag{6}$$

Here, F_{id} is the free energy of the ideal gas, E_{EG} is the ground-state energy of the degenerate electron gas, F_d is the nonlocal contribution arising from the deviation of the electron-ion pseudopotential from a purely Coulombic form, $G^{\mathrm{EC}}(q)$ is the normalized energy-wave-number characteristic, and $\Gamma_{\mathrm{eff}}=Z_{\mathrm{eff}}^2\beta/R_s$ with $Z_{\mathrm{eff}}=(Z^2-\rho_d^2)^{1/2}$, Z and ρ_d being the nominal valence and the depletion charge density, respectively. The explicit form for each of these terms can be found in Refs. 5 and 51 and is therefore not given here.

A. Two-parameter case

To carry out the two-parameter variation, the Helmholtz free energy in Eq. (6) is minimized according to the following conditions:

$$\left[\frac{\partial F}{\partial z}\right]_{n,T,\eta}=0\,,\qquad \left[\frac{\partial F}{\partial \eta}\right]_{n,T,z}=0\,. \tag{7}$$

We have denoted the charge variational parameter by z. Using Eqs. (7) and the operator identity $T(\partial/\partial T)_{n,z,\eta}=-\Gamma(\partial/\partial\Gamma)_{n,T,\eta}$, the corresponding internal energy $U_{\mathrm{CHS},2}$ and excess entropy $S_{\mathrm{CHS},2}^{\mathrm{ex}}$ can be simplified to read

$$\begin{aligned}U_{\mathrm{CHS},2}=&\frac{3}{2}k_B T+E_{\mathrm{EG}}+F_d-\frac{Z_{\mathrm{eff}}^2}{\pi}\int_0^\infty dq\, S_{\mathrm{CHS}}(q,\Gamma_m,\eta_m)G^{\mathrm{EC}}(q)\\&-k_B T\frac{\Gamma_{\mathrm{eff}}}{2\eta_m^{1/3}}\left[1+\eta_m-\frac{1}{5}\eta_m^2-\frac{1+2\eta_m}{\kappa_m}[(1+2\kappa_m\xi_m)^{1/2}-1]\right]\end{aligned} \tag{8}$$

and

$$\frac{S^{\rm ex}_{\rm CHS,2}}{k_B}=\frac{1+2\eta_m}{72\xi_m\eta_m}\{3\kappa_m\xi_m[(1+2\kappa_m\xi_m)^{1/2}+1]-2[(1+2\kappa_m\xi_m)^{3/2}-1]\}-\frac{6\eta_m}{1-\eta_m}-2\ln(1-\eta_m)\ . \tag{9}$$

Here, η_m and Γ_m in $\kappa_m=(12\eta_m^{2/3}\Gamma_m)^{1/2}$ are those determined from Eqs. (7). In the above (and in Sec. II B), $\xi_m=(1-\eta_m)^3/(1+2\eta_m)^2$. We further note that in Eq. (9) the first term on the right-hand side is the excess entropy due to charge, whereas the last two terms give the NHS entropy derived by the virial pressure method.

B. One-parameter case

In this case Γ is kept fixed and the Helmholtz free energy is required to satisfy only the condition

$$\left[\frac{\partial F}{\partial\eta}\right]_{n,T,z}=0\ . \tag{10}$$

Since $(\partial F/\partial z)_{n,T,\eta}\neq 0$, the corresponding excess entropy $S^{\rm ex}_{\rm CHS,1}$ and internal energy $U_{\rm CHS,1}$ acquire two additional contributions. We find

$$\frac{S^{\rm ex}_{\rm CHS,1}}{k_B}=\frac{S^{\rm ex}_{\rm CHS,2}}{k_B}-\frac{\Gamma Z^2_{\rm eff}}{\pi k_B T}\int_0^\infty dq\frac{\partial S_{\rm CHS}(q,\Gamma,\eta_m)}{\partial\Gamma}G^{\rm EC}(q)-\frac{(\Gamma-\Gamma_{\rm eff})(1+2\eta_m)}{4\kappa'\eta_m^{1/3}(1+2\kappa'\xi_m)^{1/2}}\times[(1+2\kappa'\xi_m)^{1/2}-(1+\kappa'\xi_m)]$$
$$=(S^{\rm ex}_{\rm CHS,2}+S^{\rm ex,(1)}_{\rm CHS,1}+S^{\rm ex,(2)}_{\rm CHS,1})/k_B \tag{11}$$

and, correspondingly,

$$U_{\rm CHS,1}=U_{\rm CHS,2}+U^{(1)}+U^{(2)}\ . \tag{12}$$

Here, η_m is the minimized parameter obtained from Eq. (10) and $\kappa'=(12\eta_m^{2/3}\Gamma)^{1/2}$, Γ being fixed *a priori* as already noted.

III. RESULTS AND DISCUSSION

We have applied Eq. (6) to the study of thermodynamic properties of four liquid alkali metals. Using the GNMP theory, we have carried out one- and two-parameter variations of F and the results are collected in Table I together with experimental data.[2,14] We now comment on the results obtained.

As can be seen from Table I, there are four closely related points that merit emphasis.

(i) The values of F obtained in the two-parameter variational calculation are lower than those obtained by minimizing F with respect to η at a value of Γ fixed theoretically by optimizing the calculated liquid structure factor.[19]

(ii) The magnitude of the plasma parameter obtained in the two-parameter variational calculation is significantly reduced, whereas the value of η_m remains virtually unchanged.

(iii) The internal energy obtained in both the one-parameter and the two-parameter calculations is in excellent agreement with experiment, but quantitatively the one-parameter calculation yields slightly better results.

(iv) In spite of the fact that the calculated structure factors in the one-parameter case (Fig. 1) are of better quality than those obtained in the two-parameter calculations (Fig. 2), the calculated excess entropies in the former case are somewhat inferior to the latter when compared with experimental data. Thus the gain in the Helmholtz free energy obtained by using two variational parameters is due to the improvement in the calculated excess entropy and occurs with a slight deterioration in the internal energy and in the liquid structure factor.

In order to examine the above points in more detail, we take Na as an example and carry out two additional one-parameter calculations at $\Gamma=209$, corresponding to the nominal ionic valence $Z=1$, and at $\Gamma=0$, corresponding to the choice of the NHS as reference system. These results are presented in Table II along with those given in Table I for $\Gamma=179$ and 45. For the purpose of illustration, further details on the internal energy and the excess entropy as functions of Γ at $\eta=\eta_m$ are included in a separate Table III. We can now understand points (i) and (ii) above if we notice from these tables that the excess entropy exhibits a clear maximum near $\Gamma=45$, thus leading to a minimum in F at a rather small value of Γ. Coming

TABLE I. Two-parameter variation results for the minimized packing fraction η_m and plasma parameter Γ_m, the internal energy $U_{{\rm CHS},i}$, the Helmholtz free energy F, and the excess entropy $S^{\rm ex}_{{\rm CHS},i}$ of liquid alkali metals near freezing. The entries in parentheses are those obtained using one-parameter variation with Γ taken from Ref. 19. The experimental data are taken from Refs. 2 and 14. All quantities are in atomic units.

Metal	Γ_m	η_m	F	$F_{\rm expt}$	$U_{{\rm CHS},i}$	$U_{\rm expt}$	$S^{\rm ex}_{{\rm CHS},i}/k_B$	$S^{\rm ex}_{\rm expt}/k_B$
Na	45	0.466	−0.2356	−0.2360	−0.227 215	−0.2320	−4.12	−3.45
	(179)	(0.467)	(−0.2354)		(−0.227 254)		(−4.31)	
K	50	0.461	−0.2009	−0.2010	−0.191 975	−0.1956	−4.06	−3.45
	(169)	(0.461)	(−0.2008)		(−0.192 005)		(−4.23)	
Rb	47	0.456	−0.1927	−0.1930	−0.183 025	−0.1870	−3.96	−3.63
	(167)	(0.456)	(−0.1926)		(−0.183 044)		(−4.14)	
Cs	59	0.460	−0.1809	−0.1820	−0.170 818	−0.1757	−4.08	−3.56
	(176)	(0.460)	(−0.1808)		(−0.170 837)		(−4.22)	

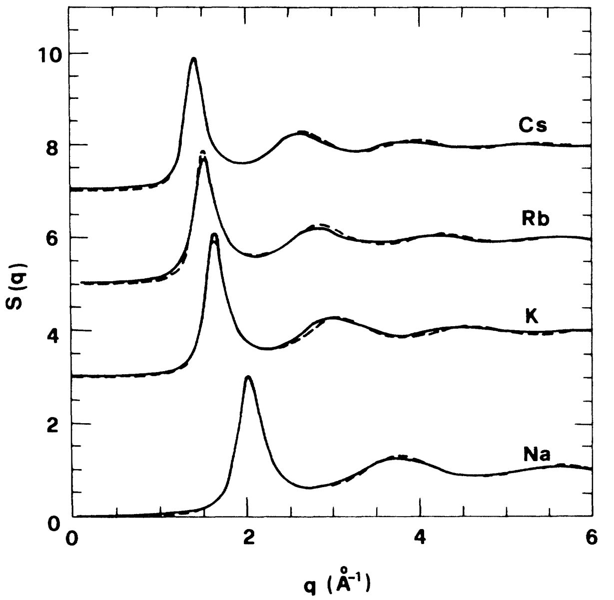

FIG. 1. Theoretical (dashed line) vs experimental (solid line) static structure factor near freezing for liquid Na, K, Rb, and Cs obtained using one-parameter variation (see text). Experimental data are taken from van der Lugt and Alblas (Ref. 55).

TABLE II. One-parameter variation results for liquid Na at freezing point. The minimized packing fraction η_m is obtained from Eq. (10). $\Gamma=0$ corresponds to the NHS model. All quantities are in atomic units.

Γ	η_m	$U_{\mathrm{CHS},1}$	$S^{\mathrm{ex}}_{\mathrm{CHS},1}/k_B$	F
209	0.470	−0.227 262	−4.38	−0.235 35
179	0.467	−0.227 256	−4.31	−0.235 43
45	0.466	−0.227 215	−4.12	−0.235 62
0	0.476	−0.227 205	−4.16	−0.235 55

to point (iii), the results for the internal energy U are not hard to understand if one recalls that for a given electronic pseudopotential U depends essentially on its structure-dependent terms. Thus the fact that U is slightly superior in the one-parameter calculation can be attributed to the somewhat more accurate structure factor (compare Figs. 1 and 2).[52] With regard to point (iv), a purely structural interpretation of the results for the excess entropy is more difficult. However, it may suffice to mention here that the behaviors that we have found for $S(q,\Gamma,\eta)$ (and hence for U) and for S^{ex} in going from one-parameter to two-parameter variational calculations parallel the behaviors that are also found when the OCP is adopted as reference system. In that case one also finds that improved agreement with measured values of S^{ex} is generally accompanied by a somewhat inferior $S(q,\Gamma)$ (for further details on OCP results, see Ref. 19).

Before drawing conclusions from the results in this section, we should emphasize two further implications that can be inferred from the above four points. First, from the relatively minor changes of $S(q,\Gamma,\eta_m)$ with Γ and the essential constancy of η_m, one verifies once again the well-known fact that the microscopic structure of a liquid metal is primarily determined by the excluded-volume effect. Second, since large variations in Γ at constant η do not alter $S(q,\Gamma,\eta)$ to a major extent (see Fig. 3) but have a significant effect on the excess entropy, we may further assert that the excess entropy of a liquid metal is sensitive to the dependence of $S(q,\Gamma,\eta)$ on Γ, whereas the internal energy is quite insensitive to global changes

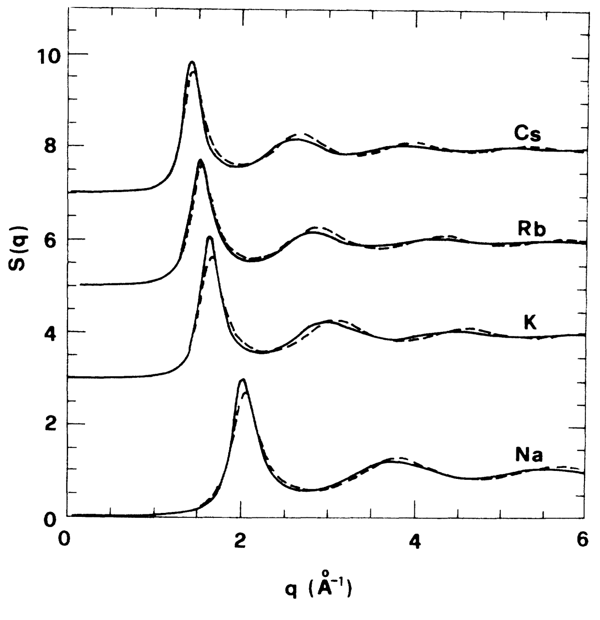

FIG. 2. Same as Fig. 1 but for two-parameter variation (see text). Refer to Fig. 1 for notation.

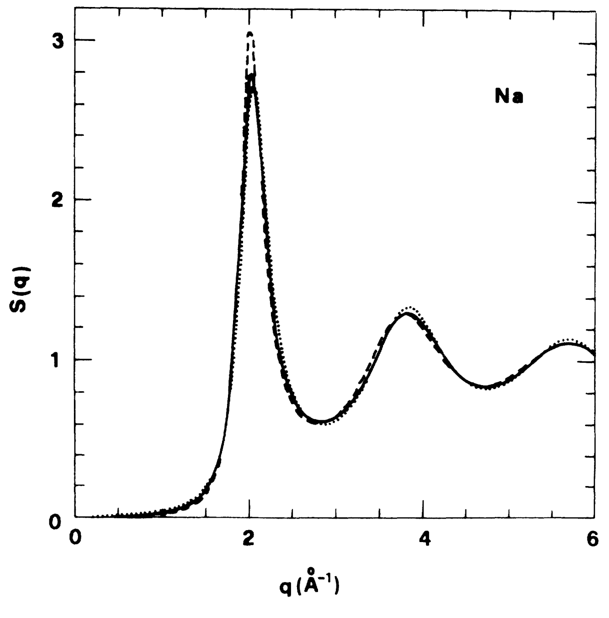

FIG. 3. Structure factor of the CHS system at $\eta=0.466$ for $\Gamma=19$ (dotted line), 99 (solid line), and 179 (dashed line).

TABLE III. One-parameter variation results for liquid Na at freezing point. The minimized packing fraction η_m is obtained from Eq. (10). $S^{\mathrm{ex}}_{\mathrm{CHS},2}$ and $S^{\mathrm{ex}(i)}_{\mathrm{CHS},1}$ are the excess entropy in the two-parameter variation and the corrections resulting from the one-parameter variation, respectively [see Eq. (11) in the text]. $U_{\mathrm{CHS},2}$ and $U^{(i)}$ are, respectively, the internal energy in the two-parameter variation and the corresponding corrections resulting from the one-parameter approximation [see Eq. (12) in the text]. All quantities are in atomic units.

Γ	η_m	$S^{\mathrm{ex}}_{\mathrm{CHS},2}/k_B$	$S^{\mathrm{ex},(1)}_{\mathrm{CHS},1}/k_B$	$S^{\mathrm{ex},(2)}_{\mathrm{CHS},1}/k_B$	$U_{\mathrm{CHS},2}$	$U^{(1)}$	$U^{(2)}$
209	0.470	−4.82	0.438	0.000	−0.227 78	0.000 52	0.000 00
179	0.467	−4.66	0.472	−0.126	−0.227 66	0.000 56	−0.000 15
45	0.466	−4.12	0.589	−0.589	−0.227 21	0.000 70	−0.000 70
0	0.476	−4.16	0.000	0.000	−0.227 20	0.000 00	0.000 00

in the structure factor of the order of those shown in Figs. 1 and 2. We explicitly note in this connection that the variations that we find in the values of U are less than 0.02%, whereas the variations of S^{ex} are of order 5%.

In conclusion, it is evident from the above results and discussion that there still are limitations in the quality of the predicted structural and thermodynamic properties even when one takes full advantage of the two disposable parameters that are available in our approach. Quantitatively we find that the calculated structure factor and excess entropy show conflicting trends. Similar difficulties arise also in variational calculations based on different choices for the reference system. Since the above conclusion holds regardless of the pseudopotential and of the expression used for F_{NHS} in Eq. (5), it is quite natural to attribute such difficulties at least partly to the approximation adopted for the excess free energy of the CHS. In this connection, we recall a remark made previously in Sec. II, where we emphasized that our expression for this quantity has been derived by the internal energy route. Although, as also mentioned there, this expression is anticipated to be the most accurate, it is nevertheless not thermodynamically consistent. This brings us then to the problem of thermodynamic self-consistency for the reference system, to which we turn in the next section.

IV. THERMODYNAMIC SELF-CONSISTENCY FOR THE CHS

In this section we discuss at some length the relationship between thermodynamic self-consistency for the reference system and the variational perturbative approach. As we stressed in Sec. III, our results for the excess entropy and internal energy, which enter the Helmholtz free energy derived by the route of the internal energy, are not mutually consistent. We attribute this conflict between S^{ex} and $S(q,\Gamma,\eta)$ to the lack of thermodynamic consistency in the excess Helmholtz free energy of the CHS reference system. Let us now look at this problem in some detail. Although we put emphasis on the charged-hard-sphere system, the argument is applicable to any hard-core-type potential.

In an interesting paper Høye and Stell[49] made a general investigation of the thermodynamics of systems with potentials of the hard-core type. According to these authors the equation of state derived in the MSA by the route of the internal energy can be shown to be

$$\beta(P^{\mathrm{IE}}-P_{\mathrm{NHS}})=\tfrac{1}{3}\pi\rho^2\sigma^3[g^2_{\mathrm{MSA}}(\sigma^+)-g^2_{\mathrm{NHS}}(\sigma^+)]+J_{\mathrm{MSA}}, \tag{13}$$

where J_{MSA} is the virial integral given by

$$J_{\mathrm{MSA}}=-\tfrac{1}{6}\beta\rho^2\sigma^3\int_{r>\sigma^+}d\mathbf{r}\,g_{\mathrm{MSA}}(r)\mathbf{r}\cdot\nabla V(r)\ . \tag{14}$$

P_{NHS} and $g_{\mathrm{NHS}}(\sigma^+)$ are the pressure and the radial distribution function at contact for the NHS system, respectively. The superscript IE in the pressure in Eq. (13) reminds us that the internal energy method has been used. This form of the equation of state can be compared directly with that obtained from the virial theorem (denoted by a superscript V), which, in terms of the *true* contact excess $\Delta h(\sigma^+)=h(\sigma^+)-h_{\mathrm{NHS}}(\sigma^+)$, $h(r)=g(r)-1$ being the total correlation function, can be written as

$$\beta(P^V-P_{\mathrm{NHS}})=\tfrac{2}{3}\pi\rho^2\sigma^3\Delta h(\sigma^+)+J\ . \tag{15}$$

Here, J has the same expression as J_{MSA} in Eq. (14) with $g_{\mathrm{MSA}}(r)$ replaced by the true radial distribution function $g(r)$. Obviously, if one approximates $g(r)$ by $g_{\mathrm{MSA}}(r)$ in Eq. (15), the result for the pressure is not thermodynamically consistent with that of Eq. (13). However, self-consistency can be imposed on these equations if one replaces the contact excess $\Delta h(\sigma^+)$ in Eq. (15) by $[g^2_{\mathrm{MSA}}(\sigma^+)-g^2_{\mathrm{NHS}}(\sigma^+)]/2$, while at the same time approximating J by J_{MSA}. This connection between internal-energy pressure and virial pressure can alternatively be viewed in the following iterative scheme, also suggested by Høye and Stell.[49]

Let us denote U_i^{IE}, J_i, and $g_i(\sigma^+)$ the ith iteration values for the configuration internal energy per particle, the integral J and the radial distribution function at contact. The corresponding Helmholtz free energy F_i^{IE} and pressure P_i^{IE} per particle can be calculated from

$$F_i^{\mathrm{IE}}=\int d\Gamma'\,U_i^{\mathrm{IE}}/\Gamma' \tag{16}$$

and

$$P_i^{\mathrm{IE}}=\rho^2\left[\frac{\partial F_i^{\mathrm{IE}}}{\partial\rho}\right]_T\ . \tag{17}$$

With these ith iteration quantities one may define $g_{i+1}(\sigma^+)$ such that

$$\tfrac{2}{3}\pi\rho^2\sigma^3 g_{i+1}(\sigma^+)=\beta P_i^{\mathrm{IE}}-\rho-J_i\ . \tag{18}$$

TABLE IV. Two-parameter variation results calculated with correction $F'_{\rm corr}$ (see text). All quantities are in atomic units.

Metal	Γ_m	η_m	F	$F_{\rm expt}$	U	$U_{\rm expt}$	$S^{\rm ex}$	$S^{\rm ex}_{\rm expt}$
Na	54	0.514	−0.2371	−0.2360	−0.2281	−0.2320	−3.61	−3.45
K	53	0.511	−0.2023	−0.2010	−0.1927	−0.1956	−3.56	−3.45
Rb	48	0.504	−0.1939	−0.1930	−0.1837	−0.1870	−3.46	−3.63
Cs	54	0.512	−0.1821	−0.1820	−0.1715	−0.1757	−3.57	−3.56

Comparison of Eq. (18) with Eq. (13) immediately suggests that, if we start from the MSA value for the pair distribution function [i.e., if we set $g_i(r)=g_{\rm MSA}(r)$ in the terms on the right-hand side of Eq. (18)], then in the next iteration we shall obtain

$$g_{i+1}(\sigma^+)=g_{\rm NHS}(\sigma^+)+\tfrac{1}{2}[g^2_{\rm MSA}(\sigma^+)-g^2_{\rm NHS}(\sigma^+)]\ . \qquad (19)$$

In principle this new value for the pair distribution function at contact, supplemented by other related thermodynamic relations such as the inverse compressibility, can be used to obtain the full $g_{i+1}(r)$ and hence the $(i+1)$-iteration values for the internal energy and the integral J (see Høye and Stell[53] for details). The iterative process can indeed be continued until a desired degree of thermodynamic self-consistency is attained. If the iterative procedure converges, thermodynamic consistency would be achieved with the viritial pressure in the form

$$\beta P^V=\tfrac{2}{3}\pi\rho^2\sigma^3 g(\sigma^+)+\rho+J\ . \qquad (20)$$

It follows from the above approach that thermodynamic consistency between internal-energy pressure and virial pressure can be improved by explicitly considering additive corrections to the pressure and to the free energy, related by $P_{\rm corr}=\rho^2(\partial F_{\rm corr}/\partial\rho)_T$. For the CHS system, characterized by the parameters Γ and η, the free-energy correction in the first iteration can be further cast in the form

$$F_{\rm corr}=2k_BT\int_0^{\eta}d\eta'[g^2_{\rm CHS}(\sigma^+;\eta',\Gamma)-g^2_{\rm NHS}(\sigma^+;\eta')]\ . \qquad (21)$$

Here,

$$g_{\rm CHS}(\sigma^+;\eta,\Gamma)=-\frac{Q^2}{24\eta}+g_{\rm NHS}(\sigma^+;\eta) \qquad (22)$$

is the CHS radial distribution function at contact in the MSA (Ref. 42) and

$$Q=\frac{1+2\eta}{1-\eta}\left[1-\left[1+\frac{2\kappa(1-\eta)^3}{(1+2\eta)^2}\right]^{1/2}\right]\ . \qquad (23)$$

Two points merit emphasis in the above results. First, we notice from Eq. (22) that for any η and Γ we have

$$g_{\rm CHS}(\sigma^+;\eta,\Gamma)<g_{\rm NHS}(\sigma^+;\eta)\ , \qquad (24)$$

so that $F_{\rm corr}$ contributes negatively to the excess Helmholtz free energy. A negative correction is consistent with the variational spirit of our approach. Second, $F_{\rm corr}$ depends on both η and Γ and the corresponding contribution to the excess entropy,

$$S_{\rm corr}=-2k_B\int_0^{\eta}d\eta'[g^2_{\rm CHS}(\sigma^+;\eta',\Gamma)-g^2_{\rm NHS}(\sigma^+;\eta')]\ , \qquad (25)$$

is always positive. Thus there is hope of variationally obtaining a larger value of Γ, which would be consistent with the liquid structure data, while at the same time compensating for the somewhat too negative values of the calculated excess entropy in Table I. This is also implied by our results for $S(q,\Gamma,\eta)$ in the one-parameter calculation (see also Fig. 1).

Having pointed out the correction which should be included in the theory in order to improve upon our present thermodynamic study, we proceed next to the question as to the possibility of evaluating $F_{\rm corr}$. To this end, a preliminary study of the integral in Eq. (21) is in order. The integral involves the difference in the contact values of two radial distribution functions. Since $S_{\rm corr}>0$ and $g_{\rm CHS}(\sigma^+;\eta,\Gamma)\to g_{\rm NHS}(\sigma^+;\eta)$ as $\Gamma\to 0$, we may physically interpret their difference as disordering arising from the charges on particles at contact. Accordingly, such a term is absent if a NHS reference system is used. In view of this, it is not theoretically justified to set $g_{\rm CHS}(\sigma^+;\eta,\Gamma)=g_{\rm NHS}(\sigma^+;\eta)$ for this term, as was done in a recent calculation by Joarder and Bari.[22] However, while there is no difficulty in the evaluation of $g_{\rm NHS}(\sigma^+;\eta)$, the MSA expression for $g_{\rm CHS}(\sigma^+;\eta,\Gamma)$ in

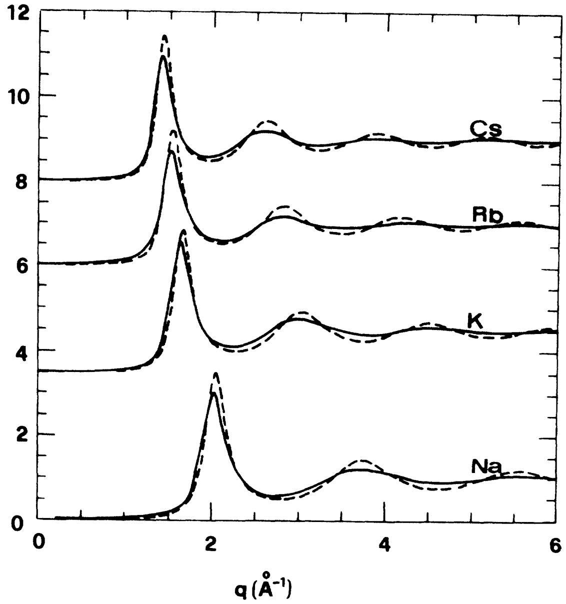

FIG. 4. Same as Fig. 1 but for two-parameter variation including additional free-energy correction (see text). Refer to Fig. 1 for notation.

TABLE V. Positions of the maxima and minima in the liquid structure factors for Na, K, Rb, and Cs at their respective melting temperature. The first, second, and third rows in each element refer, respectively, to experimental data and to calculated results in the two-parameters variation *without* and *with* free energy corrections (see text). The positions of maxima are given in the first three columns and those of minima in the last two columns. The experimental data are taken from van der Lugt and Alblas (Ref. 55).

Metal	1st	2nd	3rd	1st	2nd
Na	2.05	3.75	5.60	2.75	4.65
	2.05	3.80	5.70	2.85	4.75
	2.05	3.75	5.55	2.80	4.60
K	1.65	2.95	4.45	2.25	3.75
	1.65	3.10	4.60	2.30	3.85
	1.65	3.00	4.45	2.25	3.75
Rb	1.50	2.80	4.20	2.10	3.50
	1.55	2.90	4.30	2.15	3.60
	1.55	2.80	4.20	2.10	3.50
Cs	1.40	2.60	3.85	1.90	3.25
	1.45	2.70	4.00	2.00	3.35
	1.45	2.60	3.90	1.95	3.25

Eq. (22) is unfortunately not physically well behaved over the full range of η, but is only accurate for $\eta > 0.2$.[54] The behavior of the contact value of the radial distribution function in the CHS has been discussed by Hansen and Hayter,[54] who in their work on the static structure of a dispersion of charged colloidal particles were also faced with its evaluation at low values of the packing fraction. They proposed a rescaling recipe for dealing with unphysical negative contact values at low packing fraction. We have examined their method, but found that it is not appropriate for the present problem. We instead give a crude estimation of $F_{\rm corr}$ below, in order to gain insight into the role that it plays.

As already noted, the expression for $g_{\rm CHS}(\sigma^+;\eta,\Gamma)$ in Eq. (22) is reasonably accurate when η is larger than about 0.2. This implies that, if we split the integral in Eq. (21) into

$$\int_0^{\eta} \rightarrow \int_0^{\eta_s} + \int_{\eta_s}^{\eta} , \tag{26}$$

and are able to determine η_s such that its value is larger than about 0.2 for any given value of Γ, then we may account with reasonable accuracy for the second contribution to $F_{\rm corr}$ in Eq. (26). Among various possible approaches that we have tried for the determination of η_s, we have found that only the procedure due to Singh[29] yields the desired condition. This procedure makes use of the general property

$$c(r=0) \approx -\tfrac{4}{3}\Gamma \tag{27}$$

of the direct correlation function to determine η_s as a function of Γ. With this estimate for η_s, and ignoring the first contribution on the right-hand side of Eq. (26), we estimate

$$F_{\rm corr} \approx F'_{\rm corr} \equiv 2k_B T \int_{\eta_s}^{\eta} d\eta' [g^2_{\rm CHS}(\sigma^+;\eta',\Gamma) - g^2_{\rm NHS}(\sigma^+;\eta')] . \tag{28}$$

We emphasize that our estimate is not strictly justified, but is nevertheless useful to qualitatively examine the significance of the correction to the free energy.

The variational calculation can now be carried out by minimizing $(F + F'_{\rm corr})$ with respect to η and Γ. The results are shown in Table IV. There are two interesting aspects of these results that deserve attention. First, we see from Table IV that the excess entropies are now even closer to experiment, as is to be expected from Eq. (25). Second, the values of η_m are larger than those given in Table I, while the values of Γ_m do not change much. As consequences of the increase in η_m, we find that (a) the calculated values of the internal energy and the free energy tend towards the measured values and (b) the calculated structure factors (see Fig. 4) predict very well the positions of peaks and minima for liquid alkali metals from experiment[55] (see Table V). Thus it appears from our estimation that there is still hope for obtaining mutually consistent thermodynamic and structural results if $F_{\rm corr}$ can be properly considered. Clearly, this would best be done by transcending the MSA for the CHS reference system in a thermodynamically self-consistent approach, such as has been developed for the OCP by means of a Yukawa tail added to the MSA direct correlation function (see, e.g., Ref. 33).

V. CONCLUSION

We have reexamined the perturbative variational method based on the Gibbs-Bogoliubov inequality. Using an accurate and highly reliable nonlocal pseudopotential, we have analyzed the usefulness of the CHS system in quantitative thermodynamic studies. Our theoretical results using the CHS are of comparable quality as those obtained using the hard-sphere Yukawa reference system, but, as in earlier studies using the OCP, we find that the calculated excess entropies and the structure factors for liquid alkali metals still exhibit conflicting features. In an endeavor to understand this conflict and to move towards fully quantitative calculations, we have discussed and extended our results along the line of thermodynamic self-consistency for the CHS reference system. We find that such considerations are important if the Gibbs-Bogoliubov variational theory is to produce mutually consistent thermodynamic and structural results.

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