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Structure and thermodynamics of liquid alkali metals in variational modified hypernetted-chain theory

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The role of the Percus-Yevick hard-sphere bridge function in the modified hypernetted-chain integral equation is examined within the context of Lado's criterion [F. Lado, S. M. Foiles, and N. W. Ashcroft, Phys. Rev. A **28**, 2374 (1983)]. It is found that the commonly used Lado's criterion, which takes advantage of the analytical simplicity of the Percus-Yevick hard-sphere bridge function, is inadequate for determining an accurate static pair-correlation function. Following Rosenfeld [Y. Rosenfeld, Phys. Rev. A **29**, 2877 (1984)], we reconsider Lado's criterion in the so-called variational modified hypernetted-chain theory. The main idea is to construct a free-energy functional satisfying the virial-energy thermodynamic self-consistency. It turns out that the widely used Gibbs-Bogoliubov inequality is equivalent to this integral approach of Lado's criterion. Detailed comparison between the presently obtained structural and thermodynamic quantities for liquid alkali metals and those calculated also in the modified hypernetted-chain theory but with the one-component-plasma reference system leads us to a better understanding of the universality property of the bridge function.

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I. INTRODUCTION

In a recent paper [1], we reviewed the present status of the theoretical approach to liquid-structure calculations. Among many methods available in the literature, such as computer simulations, integral equation theories, thermodynamic variational, or perturbative approaches which include the Henderson-Barker or Weeks-Chandler-Andersen type, the Gibbs-Bogoliubov inequality, the optimized random-phase approximation, etc., we critically made a detailed comparison and came to the conclusion that the integral-equation approach based on the modified hypernetted-chain (MHNC) theory appears to be the most promising. This latter technique has been applied successfully to investigate the anomalous behavior of the liquid-structure factor of cadmium and zinc metals [1]. Similar calculations have been carried out by Pastore and Kahl [2,3] for liquid alkali metals, by Hoshino, Matsuda, and Watabe [4,5] for the expanded liquid cesium, and by Perrot and Chabrier [6] for liquid alkali and polyvalent metals. The same technique has been utilized also in a different context by Dharma-wardana and Aers [7], Aers *et al.* [8], Dharma-wardana *et al.* [9], Reatto, Levesque, and Weis [10], and Dzugutov [11] for "inverting" pair potentials for liquid metals Ge, Na, Al, and Pb. Very recently, MHNC theory has been generalized to the study of partial structure factors or liquid binary alkali-metal alloys [12].

Central to the success of the above-mentioned MHNC calculations is an appropriate choice of the bridge function $B(r)$ consisting of the sum of elementary diagrams with $h(r)$ [being the total correlation function defined by $h(r)=g(r)-1$, $g(r)$ being the static pair-correlation function] bonds that have at least triply connected field points [13]. Depending on the liquid system of interest, various forms of $B(r)$ have been proposed. The hard-sphere (HS) bridge function $B_{\rm HS}(r;\eta)$, η being the packing ratio, in particular, is one of the earliest and simplest bridge functions to be investigated. This bridge function has an attractive feature in that within the Percus-Yevick (PY) approximation $B_{\rm HS}(r;\eta)\approx B_{\rm PYHS}(r;\eta)$ can be expressed in an analytical form. Rosenfeld and Ashcroft [14] in their quantitative studies of the short-range universality property of $B(r)$ have in fact examined such a $B_{\rm PYHS}(r;\eta)$ for a wide variety of interacting potentials. They showed that excellent agreement with computer-simulation data can be obtained if the η in $B_{\rm PYHS}(r;\eta)$ is chosen appropriately. The usefulness of $B_{\rm PYHS}(r;\eta)$ has been exploited further by Rogers *et al.* [15]. These authors carried out extensive Monte Carlo simulations for the one-component-plasma system and noted that the simulated pair-correlation function can be reproduced very accurately by using $B_{\rm PYHS}(r;\eta)$. References [1–6] are several recent attempts that use also $B_{\rm PYHS}(r;\eta)$ for liquid-metallic systems. A key factor for the success of these latter works is the method they employed for determining the bridge parameter η. In this method one applies the thermodynamic-self-consistency (TSC) condition in which η is fixed by imposing the equality of the compressibilities calculated separately by the compressibility and virial-pressure equations. From the diverse potentials that have been experimented with and the success that has been achieved in each case, this TSC method can be taken as a reliable criterion.

An alternative to the TSC condition is to apply the so-called Lado's criterion [16]. In this method η is determined by minimizing an approximate free-energy functional which can be shown [16] to be equivalent to seeking an η that satisfies

$$\tfrac{1}{2}\rho\int [g^{\rm MHNC}_{\phi,{\rm PYHS}}(r;\eta)-g_{\rm PYHS}(r;\eta)]\frac{\partial B_{\rm PYHS}(r;\eta)}{\partial\eta}d\mathbf{r}=0\ ,$$

where ρ is the number density, $g^{\text{MHNC}}_{\phi,\text{PYHS}}(r;\eta)$ and $g_{\text{PYHS}}(r;\eta)$ being the static pair-correlation functions in MHNC theory for an arbitrary ϕ and a "PY" hard-sphere-like potential, respectively. Although both avenues to obtain η have been tested [1–4] and achieved varying degrees of success, Lado's criterion has received comparatively much less attention. In this paper we devote some effort to the investigation of $B(r)$ via Lado's criterion. Our motivation, besides the reason mentioned just above, stems from our observation that Lado's criterion emerges quite naturally when applied in conjunction with the widely used Gibbs-Bogoliubov inequality. It will be shown here that the latter inequality can be generalized to incorporate MHNC theory, giving rise to a powerful variational MHNC [17,18] (VMHNC) technique and permitting the simultaneous study of structural and thermodynamic properties. Compared with the above usual Lado's criterion, we draw attention in this work to a more general criterion. Specifically, we shall show [19,20] below that the usual Lado's criterion has to be augmented by an extra correction term for fixing the η bridge parameter if the analytic property of $B_{\text{PYHS}}(r;\eta)$ is to be made use of. It is also the purpose of this paper to examine this apparent difference of Lado's criterion in somewhat detail. Specifically, we demonstrate in the following that (a) the VMHNC, as advanced previously by Rosenfeld [17,18], provides a clear justification to the needed correction and thus a reliable determination of the bridge parameter η and, hence, the liquid structure is now feasible, and (b) the universal property of $B(r)$ shows up in the calculated structure and thermodynamic functions.

The format of the paper is as follows. In the next section, we review VMHNC theory and rederive all relevant formulas in the context of VMHNC theory. We discuss in this same section the use of $B_{\text{PYHS}}(r;\eta)$ in Lado's criterion *with* the correction term and $B_{\text{HS}}(r;\eta)$ *without* to outweigh their difference. Our analysis would lead us to an assessment of the reliability of the method and to the calculation of various thermodynamic functions. In Sec. III, as applications, we apply VMHNC theory to calculate the static pair-correlation function and several thermodynamic quantities for liquid alkali metals at or near freezing. We compare the theoretically Fourier-transformed $g(r)$, i.e., the liquid-structure factor $S(q)$, the calculated results for the excess entropy, and Helmholtz and internal energies, with experiments. Finally, in Sec. IV we give our conclusion.

II. VARIATIONAL MODIFIED HYPERNETTED-CHAIN THEORY

In this section we first review briefly MHNC theory and turn immediately to discuss the Gibbs-Bogoliubov inequality drawing attention to the use of a hard-sphere reference fluid. By considering the main spirit of the Gibbs-Bogoliubov inequality, we focus attention on the Percus-Yevick approximation to the hard-sphere system. This discussion will lead us naturally to the PY hard-sphere bridge function. In the spirit of VMHNC theory, we then proceed to analyze how the thermodynamic self-consistent $B_{\text{PYHS}}(r;\eta)$, which satisfies the energy-virial condition, is to be used for deriving a more general Lado's criterion.

A. Modified hypernetted-chain theory

The study of $g(r)$ as a function of temperature and density begins with the Ornstein-Zernike relation

$$h(r)=c(r)+\rho\int d\mathbf{r}\,h(|\mathbf{r}-\mathbf{r}'|)c(r)\ , \tag{1}$$

where $c(r)$ is the direct correlation function. Equation (1) is supplemented by the following closure between $h(r)$ and $c(r)$:

$$g(r)=\exp[\gamma(r)-\beta\phi(r)-B(r)]\ , \tag{2}$$

where $\phi(r)$ is the pair potential, $\beta=(k_BT)^{-1}$ is the inverse temperature, and $\gamma(r)=h(r)-c(r)$. Given a $\phi(r)$, the pair-correlation function can be obtained by solving Eqs. (1) and (2) iteratively for a prescribed bridge function $B(r)$ [the usual HNC approximation corresponds to setting $B(r)=0$].

B. Gibbs- Bogoliubov inequality

This widely used variational technique can be stated as follows. Let the liquid system of interest (being denoted by a subscript "true"), at given temperature and density, be described by the Hamiltonian H_{true}, which determines the Helmholtz free energy F_{true}:

$$\exp(-\beta F_{\text{true}})=\text{Tr}[\exp(-\beta H_{\text{true}})]\ . \tag{3}$$

If one chooses a reference system in the same thermodynamic conditions, with Hamiltonian H_{ref} and Helmholtz free energy F_{ref}, the inequality then puts an upper bound on F_{true} as

$$F_{\text{true}}\le F_{\text{ref}}+\langle H_{\text{true}}-H_{\text{ref}}\rangle_{\text{ref}}\ . \tag{4}$$

The brackets $\langle\ \rangle_{\text{ref}}$ in Eq. (4) denote a thermal average over all possible configurations of the reference system. It is clear from Eq. (4) that the inequality can be used to advantage if a judicious choice is made of the reference system. At a primitive level, one must select a reference system so that it adequately mimics basic features of the real system. A detailed discussion of the various possible reference systems can be found in our recent paper [21]. Here we wish to focus our attention on the use of a hard-sphere system. For this reference system, Eq. (4) becomes

$$\begin{aligned}F_{\text{true}}&\le F_{\text{HS}}+\langle H_{\text{true}}\rangle_{\text{HS}}-\langle H_{\text{HS}}\rangle_{\text{HS}}\\&\equiv -TS_{\text{HS}}+\langle H_{\text{true}}\rangle_{\text{HS}}\ ,\end{aligned} \tag{5}$$

where the subscript HS stands for the hard sphere and S_{HS} is the HS entropy. It is customary in the literature to evaluate the ensemble average in Eq. (5) by approximating $g_{\text{HS}}(r)$ by that derived from the PY approximation, i.e., $g_{\text{HS}}(r;\eta)\approx g_{\text{PYHS}}(r;\eta)$. This, of course, is an approximation, and the immediate consequence is that the calculated thermodynamic quantities depend on the routes to the equation of state pursued (see, for example, Table I of Hafner [22]). Now, instead of inserting $g_{\rm PYHS}(r;\eta)$, we may adopt $g_{\rm PYHS}^{\rm MHNC}(r;\eta)$ for the reference distribution function and, for consistency, carry out a corresponding substitution for the Helmholtz free energy. In this manner the accuracy of the variational calculation has been shifted to finding MHNC structural and thermodynamic functions. If, by some means, $g_{\rm PYHS}^{\rm MHNC}(r;\eta)$ were made "exact" by imposing thermodynamic-self-consistency conditions, then the subsequent calculated thermodynamic quantities will be expected to be closer to the real system. The importance of this last point in variational thermodynamic studies has in fact been stressed previously by us [21].

C. Structure and thermodynamic functions in MHNC

As pointed out in the Introduction, the PYHS bridge function determined by imposing the virial-compressibility TSC condition has been examined to predict accurately the structural and thermodynamic properties for a wide variety of disparate simple liquids. In this subsection, by appealing to the universality feature of $B(r)$, we construct a family of free-energy functionals that satisfy the virial-energy-consistency criterion and then, making use of the hard-sphere $B(r)$, variationally pick out the "best" free energy functional.

Let us start by defining a local MHNC free energy per particle for an arbitrary potential $\phi(r)$ as [23]

$$\begin{aligned}f_\phi^{\rm MHNC}(\alpha)=&\tfrac{1}{2}\rho\int d\mathbf{r}\, g_\phi^{\rm MHNC}(r;\alpha)[\beta\phi(r)+B_\phi(r;\alpha)]\\&-\tfrac{1}{2}\rho\int d\mathbf{r}\{\tfrac{1}{2}[h_\phi^{\rm MHNC}(r;\alpha)]^2+h_\phi^{\rm MHNC}(r;\alpha)-g_\phi^{\rm MHNC}(r;\alpha)\ln g_\phi^{\rm MHNC}(r;\alpha)\}\\&-\frac{1}{2\rho}\frac{1}{(2\pi)^3}\int d\mathbf{k}\{\ln[1+\rho\tilde{h}_\phi^{\rm MHNC}(k;\alpha)]-\rho\tilde{h}_\phi^{\rm MHNC}(k;\alpha)\}\ ,\end{aligned}\tag{6}$$

where the tildes refer to the Fourier transform, α is a parameter associated with the bridge function $B_\phi(r;\alpha)$, and the subscript ϕ designates the quantity obtained iteratively from Eqs. (1) and (2) with the exact bridge function $B_\phi(r;\alpha)$ and $\phi(r)$. For convenience in the following discussion we also define a function

$$\Delta_\phi^{\rm MHNC}(\alpha)=\tfrac{1}{2}\rho\int_0^\alpha d\alpha'\int d\mathbf{r}\, g_\phi^{\rm MHNC}(r;\alpha')\frac{\partial B_\phi(r;\alpha')}{\partial\alpha'}\ .\tag{7}$$

To proceed, we note first of all that the energy equation of state can be written

$$u=\tfrac{1}{2}\beta\rho\int d\mathbf{r}\, g_\phi^{\rm MHNC}(r;\alpha)\phi(r)\ ,\tag{8}$$

while the virial-pressure equation of state reads

$$\left[\frac{\beta P}{\rho}\right]_{\rm virial}=1-\frac{\beta}{6}\rho\int d\mathbf{r}\, r g_\phi^{\rm MHNC}(r;\alpha)\frac{\partial\phi(r)}{\partial r}\ .\tag{9}$$

At given temperature and density [i.e., for a nonvanishing $B_\phi(r;\alpha(\beta,\rho))$], the excess free energy per particle, $\mathcal{F}$, can be obtained directly from Eqs. (8) and (9) and expressed in terms of Eqs. (6) and (7) as [18]

$$\mathcal{F}_\phi^E=f_\phi^{\rm MHNC}(\alpha)-\int_0^\beta d\beta'\frac{\partial\alpha(\beta',\rho)}{\partial\beta'}\times\left.\frac{\partial\Delta_\phi^{\rm MHNC}(\beta',\rho;\alpha)}{\partial\alpha}\right|_{\alpha=\alpha(\beta',\rho)}\ ,\tag{10}$$

$$\mathcal{F}_\phi^V=f_\phi^{\rm MHNC}(\alpha)-\int_0^\rho d\rho'\frac{\partial\alpha(\beta,\rho')}{\partial\rho'}\times\left.\frac{\partial\Delta_\phi^{\rm MHNC}(\beta,\rho';\alpha)}{\partial\alpha}\right|_{\alpha=\alpha(\beta,\rho')}\ ,\tag{11}$$

where the superscripts E and V mean, respectively, quantities derived from energy and virial equations of state. Since an evaluation of the exact functional expression for $B_\phi(r;\alpha)$ is practically impossible, we consider two alternatives. We can either take advantage of the universality property of bridge function and proceed with an analytic $B_\phi(r;\alpha)=B_{\rm PYHS}(r;\eta)$, but this would need an appropriate "correction" which accounts for the possible difference between the HS and PYHS, or one may adopt the HS theory [24,25] $B_\phi(r;\alpha)=B_{\rm HS}(r;\eta)$, which is known to reproduce well the computer simulation. We discuss separately the essence of these methods.

In the first approach, one begins by introducing a variational free-energy functional $\mathcal{F}_\phi^{\rm VMHNC}(\eta)$, defined by

$$\mathcal{F}_\phi^{\rm VMHNC}(\eta)=f_\phi^{\rm MHNC}(\eta)-\Delta_\phi^{(0)}(\eta)\ ,\tag{12}$$

where, for the moment, $f_\phi^{\rm MHNC}(\eta)$ is given by Eq. (6) with $B_\phi(r;\alpha)\equiv B_{\rm HS}(r;\eta)$ [making use of the universality characteristic of $B(r)$] and $\Delta_\phi^{(0)}(\eta)$ is a "fitting" function having the following two features. In the first place, it must satisfy the physical condition $\Delta_\phi^{(0)}(\eta=0)=0$ so that the correct description of the structure and thermodynamics using MHNC theory for low-density behaviors is ensured. Second, in accordance with the spirit of perturbation, $\Delta_\phi^{(0)}(\eta)$ must be separable into a "main" function that is independent of the details of potential [for which the universality feature of $B(r)$ can be fully made use of] plus the remaining terms which depend on the potential and account for the difference stated above. Since Eq. (6) for $\alpha=\eta$ can be easily shown to satisfy [23]

$$\left.\frac{\partial f_\phi^{\mathrm{MHNC}}(\eta)}{\partial\eta}\right|_{\beta,\rho}=\tfrac{1}{2}\rho\int d\mathbf{r}\,g_\phi^{\mathrm{MHNC}}(r;\eta)\frac{\partial B_{\mathrm{HS}}(r;\eta)}{\partial\eta}\equiv\frac{\partial}{\partial\eta}\Delta_\phi^{\mathrm{MHNC}}(\eta)\ , \tag{13}$$

it is natural to write

$$\Delta_\phi^{(0)}(\eta)=\Delta_\phi^{\mathrm{MHNC}}(\eta)=\tfrac{1}{2}\rho\int_0^\eta d\eta'\int d\mathbf{r}\,g_\phi^{\mathrm{MHNC}}(r;\eta')\frac{\partial B_{\mathrm{HS}}(r;\eta')}{\partial\eta'}\ , \tag{14}$$

which we assume to be a criterion for determining η. Note that in Eqs. (13) and (14) we have replaced $B_\phi(r;\alpha)$ by $B_{\mathrm{HS}}(r;\eta)$ in view of the universal property of the bridge function. It can be shown [18,23] that Eqs. (12) and (14) obey Hiroike's test [26] $(\partial u/\partial V)_T=T(\partial P/\partial T)_V-P$ and thus ensure the energy and virial equations, given by Eqs. (10) and (11) respectively, to be thermodynamically self-consistent. Furthermore, Eqs. (13) and (14) also imply

$$\frac{\partial}{\partial\eta}\mathcal{F}_\phi^{\mathrm{VMHNC}}(\eta)=0\ . \tag{15}$$

Our next task is to find a $\Delta_\phi^{(0)}(\eta)$ which takes full benefit of the analytic simplicity of $B_{\mathrm{PYHS}}(r;\eta)$ given by [14]

$$B_{\mathrm{PYHS}}(r;\eta)=\begin{cases}-c_{\mathrm{PYHS}}(r;\eta)-1-\ln[-c_{\mathrm{PYHS}}(r;\eta)]\ , & r<\sigma\\ g_{\mathrm{PYHS}}(r;\eta)-1-\ln g_{\mathrm{PYHS}}(r;\eta)\ , & r>\sigma\end{cases} \tag{16}$$

$\sigma=(6\eta/\pi\rho)^{1/3}$ being the hard-sphere diameter. To this end we follow Rosenfeld [18] and approximate

$$\Delta_\phi^{(0)}(\eta)\approx\Delta_{\phi,\mathrm{PYHS}}^{(0)}(\eta)=\tfrac{1}{2}\rho\int_0^\eta d\eta'\int d\mathbf{r}\,g_{\phi,\mathrm{PYHS}}^{\mathrm{MHNC}}(r;\eta')\frac{\partial B_{\mathrm{PYHS}}(r;\eta')}{\partial\eta'}\ , \tag{17}$$

so that Eq. (12) should accordingly be written

$$\mathcal{F}_\phi^{\mathrm{VMHNC}}(\eta)\approx f_{\phi,\mathrm{PYHS}}^{\prime\mathrm{MHNC}}(\eta)-\Delta_{\phi,\mathrm{PHYS}}^{(0)}(\eta)\ . \tag{18}$$

Here $g_{\phi,\mathrm{PYHS}}^{\mathrm{MHNC}}(r;\eta)$ is the iterative solution of Eqs. (1) and (2) for the potential $\phi(r)$ and bridge function $B_{\mathrm{PYHS}}(r;\eta)$, and $f_{\phi,\mathrm{PYHS}}^{\prime\mathrm{MHNC}}(\eta)$, except for the substitution of $B_\phi(r;\alpha)$ by $B_{\mathrm{PYHS}}(r;\eta)$ thus resulting in $g_\phi^{\mathrm{MHNC}}(r;\eta)\to g_{\phi,\mathrm{PYHS}}^{\mathrm{MHNC}}(r;\eta)$, has the same form as Eq. (6). Following the recipe mentioned above Eq. (13), we write

$$\Delta_{\phi,\mathrm{PYHS}}^{(0)}(\eta)=\Delta_{\mathrm{PYHS}}(\eta)-\delta_\phi(\eta)\ . \tag{19}$$

In Eq. (19), $\Delta_{\mathrm{PYHS}}(\eta)$ is the above-mentioned "main" (potential-independent) function having the same mathematical form as $\Delta_\phi^{\mathrm{MHNC}}(\eta)$ [see Eq. (14)], but with $g_\phi^{\mathrm{MHNC}}(r;\eta)$ and $B_{\mathrm{HS}}(r;\eta)$ occurring there replaced by $g_{\mathrm{PYHS}}(r;\eta)$ and $B_{\mathrm{PYHS}}(r;\eta)$, respectively. In this way $\delta_\phi(\eta)$ is the necessary correction term emphasized below Eq. (12) that characterizes the deviation of PYHS (corresponding to some "PY" potential) from HS [corresponding to the use of an exact HS $B_{\mathrm{HS}}(r;\eta)$ and potential $\phi(r)$].

To make further progress, we note that $\Delta_{\mathrm{PYHS}}(\eta)$ can be written in analogy to Eq. (12) as

$$\mathcal{F}_{\mathrm{PYHS}}^{\mathrm{VMHNC}}(\eta)=f_{\mathrm{PYHS}}^{\mathrm{MHNC}}(\eta)-\Delta_{\mathrm{PYHS}}(\eta)\ , \tag{20}$$

where $f_{\mathrm{PYHS}}^{\mathrm{MHNC}}(\eta)$ differs from $f_{\phi,\mathrm{PYHS}}^{\prime\mathrm{MHNC}}(\eta)$ introduced in Eq. (18) by having the "PY" potential and associated $g_{\mathrm{PYHS}}(r;\eta)$ instead of $\phi(r)$ and $g_{\phi,\mathrm{PYHS}}^{\mathrm{MHNC}}(r;\eta)$. The "virial" part of the free energy, $\mathcal{F}_{\mathrm{PY},V}(\eta)$, can be written [27,28]

$$\mathcal{F}_{\mathrm{PYHS}}^{\mathrm{VMHNC}}(\eta)=\mathcal{F}_{\mathrm{PY},V}(\eta)=\frac{6\eta}{1-\eta}+2\ln(1-\eta)\ . \tag{21}$$

By virtue of Eqs. (18)–(21), the VMHNC free energy reads

$$\mathcal{F}_\phi^{\mathrm{VMHNC}}(\eta)=\mathcal{F}_{\mathrm{PY},V}(\eta)-f_{\mathrm{PYHS}}^{\mathrm{MHNC}}(\eta)+\delta_\phi(\eta)+f_{\phi,\mathrm{PYHS}}^{\prime\mathrm{MHNC}}(\eta)=-\Delta_{\mathrm{PYHS}}(\eta)+\delta_\phi(\eta)+f_{\phi,\mathrm{PYHS}}^{\prime\mathrm{MHNC}}(\eta)\ , \tag{22}$$

which, from Eqs. (13) and (15), leads to an equation for determining η:

$$\frac{\partial}{\partial\eta}\mathcal{F}_\phi^{\mathrm{VMHNC}}(\eta)=\frac{\partial\delta_\phi(\eta)}{\partial\eta}+\tfrac{1}{2}\rho\int d\mathbf{r}[g_{\phi,\mathrm{PYHS}}^{\mathrm{MHNC}}(r;\eta)-g_{\mathrm{PYHS}}(r;\eta)]\frac{\partial B_{\mathrm{PYHS}}(r;\eta)}{\partial\eta}=0\ . \tag{23}$$

At this point there are two important observations that merit emphasis. First, it can now be seen that we recover the usual Lado's criterion if we set $\delta_\phi(\eta)=0$. Second, the minimization of the Helmholtz free energy given by Eq. (5) turns out to be equivalent to the presently obtained Lado's criterion, as is proved in the Appendix. It is also interesting to note that when $\delta_\phi(\eta)=0$, the VMHNC results for hard spheres will reduce to that for a PY approximation for hard spheres [as implied by Eqs. (18)–(20)]. We finally turn to $\delta_\phi(\eta)$.

Strictly speaking, $\delta_\phi(\eta)$ is a function depending on details of the $\phi(r)$ potential via $g_\phi^{\mathrm{MHNC}}(r;\eta)$ in the iterative solution of Eqs. (1) and (2). A close examination of Eqs. (14) and (17) for the sequence of approximations from HS to PYHS, however, points to the fact that $\delta_\phi(\eta)$ is essentially a function characterizing the difference between the HS and "PY" potentials. Accordingly, a reasonable estimation for $\delta_\phi(\eta)$ can be obtained if one recalls that the Carnahan-Starling (CS) [29] free energy reproduces very accurately the computer-simulation data for hard spheres. Bearing in mind the above observations, we may approximate $\delta_\phi(\eta)\approx\delta_{\rm HS\text{-}PYHS}(\eta)$ and write, as in Eq. (20),

$$\mathcal{F}_{\rm CS}^{\rm VMHNC}(\eta)=f_{\rm CS}^{\rm MHNC}(\eta)-\Delta_{\rm CS}(\eta)\ , \tag{24}$$

where

$$\Delta_{\rm CS}(\eta)=\tfrac{1}{2}\rho\int_0^\eta d\eta'\int d\mathbf{r}\, g_{\rm HS}(r;\eta')\frac{\partial B_{\rm HS}(r;\eta')}{\partial\eta'}\ . \tag{25}$$

Note that $g_{\rm HS}(r;\eta)$ and $B_{\rm HS}(r;\eta)$ are, respectively, the (close to) "exact" HS pair-correlation and bridge functions (in view of the use of Carnahan-Starling free energy), for which we may take the Verlet-Weis [24] Henderson-Grundke [25] theory for their evaluation. Writing

$$\mathcal{F}_{\rm CS}^{\rm VMHNC}(\eta)=\mathcal{F}_{\rm CS}(\eta) =\frac{4\eta-3\eta^2}{(1-\eta)^2}\ , \tag{26}$$

we obtain

$$f_{\rm CS}^{\rm MHNC}(\eta)=\mathcal{F}_{\rm CS}(\eta)+\Delta_{\rm CS}(\eta)\ . \tag{27}$$

Taking the difference between Eqs. (20) and (24), it is straightforward to show that

$$f_{\rm CS}^{\rm MHNC}(\eta)-f_{\rm PYHS}^{\rm MHNC}(\eta)=\mathcal{F}_{\rm CS}(\eta)-\mathcal{F}_{{\rm PY},v}(\eta) +\Delta_{\rm CS}(\eta)-\Delta_{\rm PYHS}(\eta)\ . \tag{28}$$

Approximating $\Delta_{\rm CS}(\eta)$ by substituting $B_{\rm HS}(r;\eta)$ for the analytical $B_{\rm PYHS}(r;\eta)$,

$$\Delta_{\rm CS}(\eta)\approx\Delta'_{\rm CS}(\eta) =\tfrac{1}{2}\rho\int_0^\eta d\eta'\int d\mathbf{r}\, g_{\rm HS}(r;\eta')\frac{\partial B_{\rm PYHS}(r;\eta')}{\partial\eta'}\ , \tag{29}$$

the $\Delta_{\rm CS}(\eta)-\Delta_{\rm PYHS}(\eta)$ on the right-hand side should be reasonably approximated from Eqs. (17) and (19) as

$$\begin{aligned}\Delta_{\rm CS}(\eta)-\Delta_{\rm PYHS}(\eta)&\approx\Delta'_{\rm CS}(\eta)-\Delta_{\rm PYHS}(\eta)\\ &=\Delta^{(0)}_{\phi,{\rm PYHS}}(\eta)-\Delta_{\rm PYHS}(\eta)\\ &=-\delta_{\rm HS\text{-}PYHS}(\eta)\ ,\end{aligned} \tag{30}$$

where, again based on the universality of $B(r)$, we have written $g_{\rm HS}(r;\eta)\equiv g^{\rm MHNC}_{\phi,{\rm PYHS}}(r;\eta)$. On the other hand, the left-hand side of Eq. (28), which is essentially the difference in the MHNC free energies corresponding to the "PY" and HS potentials, is expected to be very small. Accordingly, we arrive at

$$\delta_{\rm HS\text{-}PYHS}(\eta)=\mathcal{F}_{\rm CS}(\eta)-\mathcal{F}_{\rm PY,v}(\eta)\ . \tag{31}$$

This is the $\delta_{\rm HS\text{-}PYHS}(\eta)$ that we shall use in the following application. A similar $\delta_{\rm HS\text{-}PYHS}(\eta)$ expression has been derived by Rosenfeld [17,18] in both an analytical and a

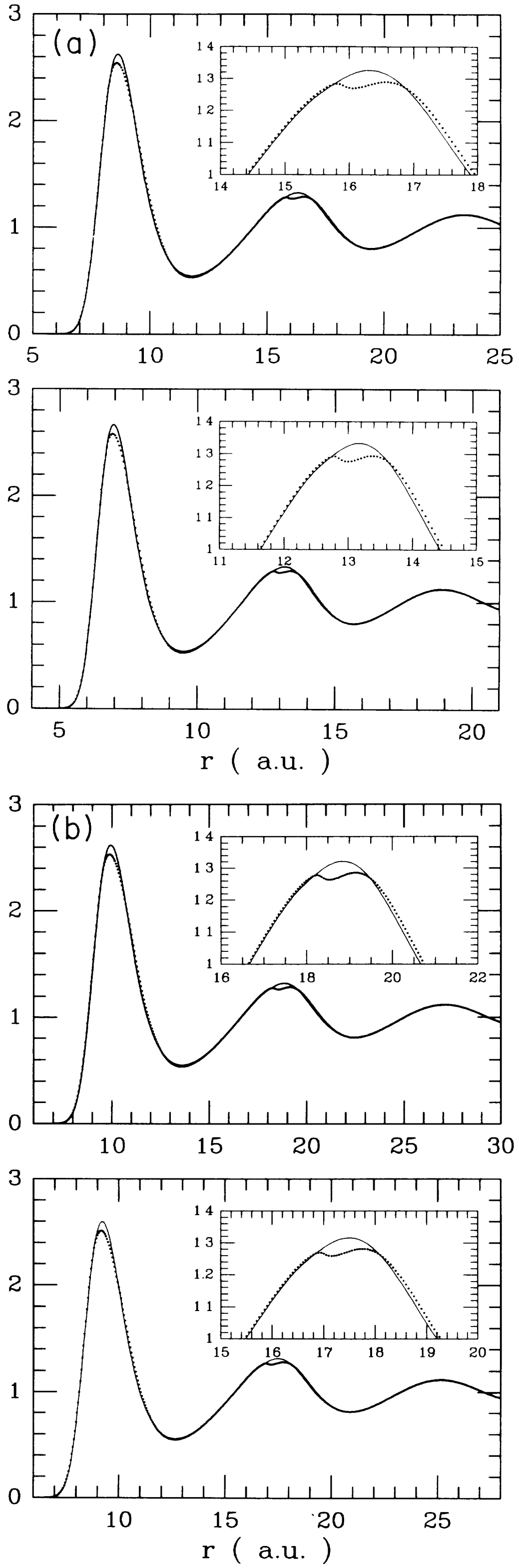

FIG. 1. (a) Static pair-correlation function $g(r)$ calculated in MHNC theory for liquid K (top) and Na (bottom) metals at or near freezing. The insets in each figure display the "kink" as discussed in text. Notations used are the following: MHNC theory using Eq. (23), solid curve; MHNC theory using Eq. (34), solid circles. (b) Same as (a) except that the top figure refers to liquid Cs and the bottom figure to liquid Rb metal. Notations of the curves are the same as in (a).

more "pictorial" way.

We come next to discuss the second method. In this method one notes first of all that the variation MHNC free energy can be written

$$\mathcal{F}_{\phi}^{\mathrm{VMHNC}}(\eta)=f_{\phi}^{\mathrm{MHNC}}(\eta)-\Delta_{\mathrm{HS}}(\eta)\ , \qquad (32)$$

where $\Delta_{\mathrm{HS}}(\eta)$ is the same as Eq. (7), but with the $g_{\phi}^{\mathrm{MHNC}}(r;\alpha=\eta)$ and $B_{\phi}(r;\alpha=\eta)$ [for a physical potential $\phi(r)$] replaced by $g_{\mathrm{HS}}(r;\eta)$ and $B_{\mathrm{HS}}(r;\eta)$ (for a HS potential), respectively. Guided by Eqs. (13) and (14), we now assume

$$\begin{aligned}\Delta_{\mathrm{HS}}(\eta)&=\Delta_{\phi}^{\mathrm{MHNC}}(\eta)\\&=\tfrac{1}{2}\rho\int_{0}^{\eta}d\eta'\int d\mathbf{r}\,g_{\phi,\mathrm{HS}}^{\mathrm{MHNC}}(r;\eta')\frac{\partial B_{\mathrm{HS}}(r;\eta')}{\partial\eta'}\ ,\end{aligned} \qquad (33)$$

which one can easily see from Eq. (15) and the definitions of Δ_{HS} and $\Delta_{\phi}^{\mathrm{MHNC}}(r;\eta)$ that

$$\begin{aligned}\frac{\partial}{\partial\eta}\mathcal{F}_{\phi}^{\mathrm{VMHNC}}(\eta)=\tfrac{1}{2}\rho\int d\mathbf{r}[g_{\phi,\mathrm{HS}}^{\mathrm{MHNC}}(r;\eta)-g_{\mathrm{HS}}(r;\eta)]\\ \times\frac{\partial B_{\mathrm{HS}}(r;\eta)}{\partial\eta}=0\ .\end{aligned} \qquad (34)$$

This is another criterion which Lado, Foiles, and Ashcroft [16] obtained previously and that can also serve as an alternative means for fixing η. We stress, in particular, two important points. First, $g_{\mathrm{HS}}(r;\eta)$ in $\Delta_{\mathrm{HS}}(\eta)$ of Eq. (32) corresponds to the exact hard-sphere pair-correlation function such as those given in Refs. [24] and [25]. Second, we have explicitly made use of the universality of $B(r)$ in making the assumption expressed by Eq. (33). This, or more explicitly Eq. (34), should yield the same result for the static pair-correlation function as that given by Eq. (23), although the bridge parameter η determined may not be the same. It is imperative to note also that the solutions for η calculated with and without $\delta_{\mathrm{HS\text{-}PYHS}}(\eta)$ constitute different versions but similar approximations to the final $g_{\phi}^{\mathrm{MHNC}}(r;\eta)$ obtained. We present liquid-structure results calculated separately in the next section.

Having discussed the criterion for determining the bridge parameter, the thermodynamic functions can be written down readily. First, as mentioned below Eq. (23) and proved in Appendix, the metallic Helmholtz free energy is given by

$$\beta F=\beta F_{\mathrm{gas}}+\beta u(n_0)+\mathcal{F}^{\mathrm{VMHNC}}(\eta)\ , \qquad (35)$$

where F_{gas} is the ideal-gas free energy per particle and

$$\begin{aligned}u(n_0)=E_{\mathrm{EG}}+E_d-2\pi\rho Z_{\mathrm{eff}}^{2}\lim_{q\to0}\frac{1-G_N^{\mathrm{EC}}(q)}{q^2}\\-\frac{1}{\pi}\int_0^{\infty}dq\,\rho_d^2|M(q)|^2-\frac{Z_{\mathrm{eff}}^2}{\pi}\int_0^{\infty}dq\,G_N^{\mathrm{EC}}(q)\ ,\end{aligned} \qquad (36)$$

being the structure-independent energy. Here E_{EG} is the electronic ground-state energy; E_d is the nonlocal contribution arising from the deviation of electron-ion pseudopotential from purely Coulombic form; $G_N^{\mathrm{EC}}(q)$ is the usual normalized energy wave-number characteristic, which, in the modified model potential theory of Li, Li, and Wang [30], now includes a high-order-perturbation correction $Z_{\mathrm{eff}}^2=Z^2-\rho_d^2$, Z and ρ_d being, respectively, the nominal valence and depletion charge density; and, finally, $M(q)$ is the Fourier transform of the depletion-hole-charge distribution [31]. The detailed expressions for each can be found in the works of Lai, Matsuura, and Wang [32] and Wang and Lai [33], and given an electronic density all these terms can be calculated straightforwardly. The internal energy per particle, U, and the excess entropy per particle, $s_{\mathrm{MHNC}}^{\mathrm{ex}}$, can be derived similarly from F, given by

$$U=\tfrac{3}{2}k_BT+u(n_0)+2\pi\rho\int_0^{\infty}dr\,r^2\phi(r)g_{\phi}^{\mathrm{MHNC}}(r;\eta) \qquad (37)$$

and Eq. (A1) in the Appendix, respectively.

TABLE I. Temperature T (K), atomic volume Ω_0, packing fraction η, plasma parameter Γ, Helmholtz free energy F, internal energy U, and excess entropy $s_{\mathrm{MHNC}}^{\mathrm{ex}}=-S_{\mathrm{MHNC}}^{\mathrm{ex}}/Nk_B$ for liquid alkali metals near freezing. The data in the last row for each liquid metal refer to results obtained using the MHNC OCP as reference system (see text for details).

Metal	η/Γ	T	Ω_0	F	F_{expt}[c]	U	U_{expt}[c]	$s_{\mathrm{MHNC}}^{\mathrm{ex}}$	s_{expt}[c]
Na	0.4643[a]	373	277.9	−0.235 19	−0.2360	−0.227 21	−0.2320	−4.47	−3.45
	0.4957[b]			−0.235 16		−0.227 19		−4.47	
	141			−0.235 8		−0.227 0		−3.75	
K	0.4621[a]	336	528.5	−0.200 72	−0.2010	−0.191 98	− 0.1956	−4.30	−3.45
	0.4950[b]			−0.200 70		−0.191 97		−4.31	
	140			−0.201 2		−0.191 8		−3.74	
Rb	0.4578[a]	312	654.6	−0.192 40	−0.1930	−0.183 10	−0.1870	−4.39	−3.63
	0.4923[b]			−0.192 39		−0.183 11		−4.41	
	138			−0.192 9		−0.183 0		−3.71	
Cs	0.4638[a]	302	810.8	−0.180 68	−0.1820	−0.170 85	−0.1757	−4.34	−3.56
	0.4998[b]			−0.180 66		−0.170 87		−4.37	
	140			−0.181 1		−0.170 7		−3.74	

[a] Bridge parameters determined from Eq. (23).

[b] Bridge parameters determined from Eq. (34).

[c] Consult Ref. [41] for sources.

III. APPLICATION: LIQUID ALKALI METALS

Equations (23) and (34) have been applied to determine the bridge parameters η for liquid alkali metals. To solve the MHNC $g(r)$ we require the metallic pair potential $\phi(r)$ and an algorithm for solving Eqs. (1) and (2). For the former we use the generalized nonlocal model pseudopotential of Li, Li, and Wang [30] as this has been checked to be quite accurate and reliable. For the latter we have adopted, as in our recent work [1], the efficient algorithm proposed previously by Gillan [34]. Figures 1(a) and 1(b) display $g_{\phi}^{\mathrm{MHNC}}(r;\eta)$ for four liquid alkali metals Na, K, Rb, and Cs at or near freezing, calculated using the two versions of Lado's criterion, namely, Eqs. (23) and (34). The corresponding thermodynamic functions along with the input data are, however, documented in Table I. There are two interesting features that can be learned from these figures and data.

(1) Apart from noticeable "kinks" at the second maxima [see the inset in Figs. 1(a) and 1(b)], the difference between $g_{\phi,\mathrm{PYHS}}^{\mathrm{MHNC}}(r;\eta)$ [from Eq. (23)] and $g_{\phi,\mathrm{HS}}^{\mathrm{MHNC}}(r;\eta)$ [from Eq. (34)] is insignificantly small, overall amounting to less than 1%.

(2) The Helmholtz and internal energies all agree very well with measured values, but the excess entropies compare less favorably with observed data.

The first point is of no surprise if one recalls the well-known defect of the Verlet-Weis-Henderson-Grundke HS theory for $g(r)$. Note that despite the fact that we use different Lado's criteria for fixing the bridge parameter η, the final MHNC results do not differ very much. To further support our presently obtained $g_{\phi}^{\mathrm{MHNC}}(r;\eta)$ quantitatively, we Fourier-transform the latter and compare the $S_{\phi}^{\mathrm{MHNC}}(q;\eta)$ in Figs. 2(a) and 2(b) with x-ray-diffraction data. We find excellent agreement with experiments for all four $S_{\phi}^{\mathrm{MHNC}}(q;\eta)$. Nevertheless, the liquid-structure factor calculated without $\delta_{\mathrm{HS\text{-}PYHS}}(\eta)$ in Eq. (23), for which the bridge parameters $\eta_{\mathrm{Na}}=0.5078$, $\eta_{K}=0.5058$, $\eta_{\mathrm{Rb}}=0.5008$, and $\eta_{\mathrm{Cs}}=0.5064$, as were widely employed by other researchers [4], show larger discrepancies [cf. Figs. 3(a) and 3(b)]. From this comparison it is thus clear that the usual Lado's criterion [without $\delta_{\mathrm{HS\text{-}PYHS}}(\eta)$] is inadequate if one were to employ the analytical $B_{\mathrm{PYHS}}(r;\eta)$ in MHNC theory. On the other hand, the success of the present version of Lado's criterion indicates once more the high quality of the MHNC approach to $S(q)$.

Coming to the second point, these F and U results are due to a much improved $g_{\phi}^{\mathrm{MHNC}}(r;\eta)$ occurring explicitly in the structure-dependent terms. Although VMHNC theory presented here attempts to resolve part of the ambiguities associated with an approximate $g(r)$ that leads to different routes to the equation of state [22] and hence reference thermodynamic functions, the calculated excess entropy $s_{\mathrm{MHNC}}^{\mathrm{ex}}$ has not been improved concurrently with $S_{\phi}^{\mathrm{MHNC}}(q;\eta)$. In other words, by merely preserving the thermodynamic energy-virial self-consistency condition in MHNC theory, the full reliability of the reference system adopted is not guaranteed. This opposition in trends between s^{ex} and $S(q)$, however, reminds us of the widely used Gibbs-Bogoliubov variational calculation using the

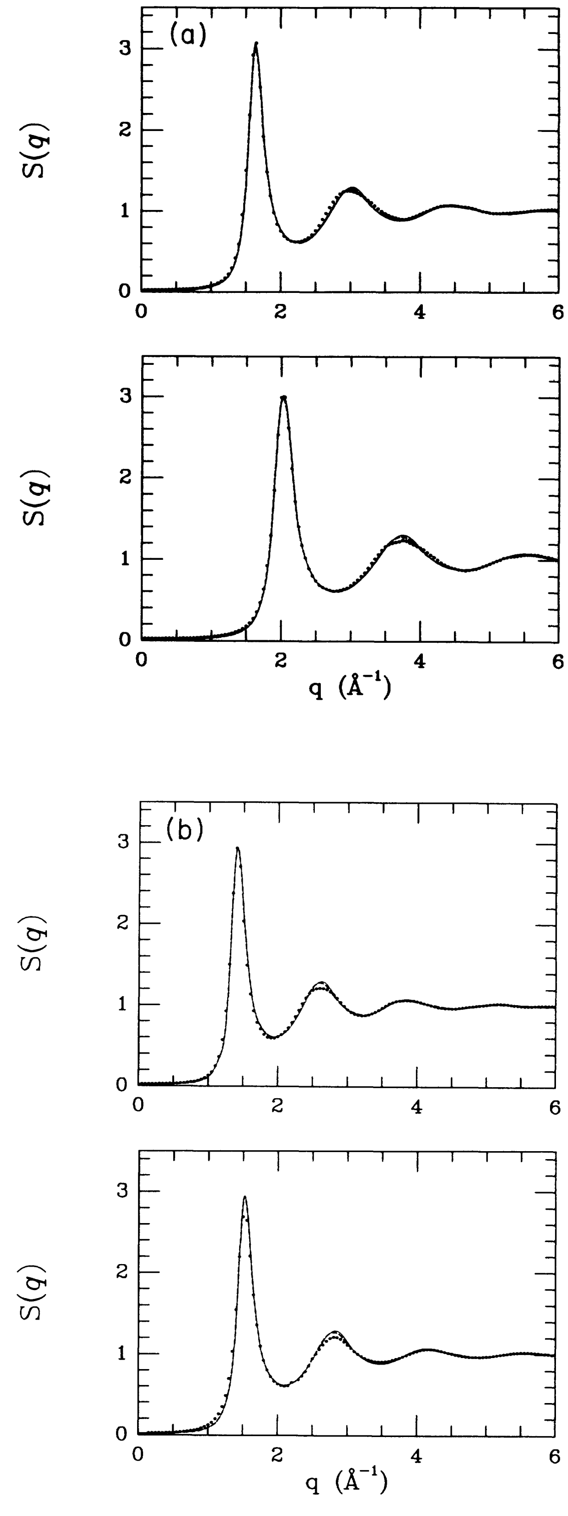

FIG. 2. Static liquid-structure factor $S(q)$ calculated by Fourier-transforming $g(r)$ given in Fig. 1(a). The top and bottom figures refer, respectively, to liquid K and Na metals at or near freezing. Experimental data (denoted by solid circles) from Ref. [44] are included for comparison. Notations used are the following: MHNC theory using Eq. (23), solid curve; MHNC theory using Eq. (34), dashed curve. (b) Same as (a) except that the top figure refers to liquid Cs and the bottom figure to liquid Rb metal. Notations of the curves are the same as in (a).

one-component plasma (OCP) as a reference system. In some of the early published works [35–37], the $S_{\rm OCP}(q;\Gamma)$, Γ being the plasma parameter, which is needed to evaluate the second term on the right-hand of Eq. (4), is normally obtained from extensive simulation data [38,39]. In recent years, for practical reasons, there have been attempts [40–42] to employ a substitution for $S_{\rm OCP}(q;\Gamma)$. Rogers *et al.* [15] first furnished such an accurate liquid-structure factor by applying MHNC theory along with the virial-compressibility TSC condition. Except for the criterion in determining η, this MHNC liquid-structure calculation of Rogers *et al.* is technically similar to the VMHNC theory presented in this work, where we solve for the $g_{\phi}^{\rm MHNC}(r;\eta)$ with a realistic $\phi(r)$ instead of the $g_{\rm OCP}^{\rm MHNC}(r;\Gamma)$ determined iteratively with an OCP potential. The implication of this fact is that, if the bridge function is indeed universal and independent of the interacting potential, the quality of the predicted thermodynamic functions in either case should not differ very much. In order to demonstrate our viewpoint, we include in Table I the related structural and thermodynamic quantities [41] calculated using $S_{\rm OCP}^{\rm MHNC}(q;\Gamma)$ [15] and the reference free energy which is *integrated* from the Monte Carlo internal energy [39]. It can be seen immediately that a deteriorated $S(q)$ (see also Fig. 4) leads to an improvement of $s^{\rm ex}$ and vice versa. To elaborate our argument further, we also arbitrarily [43] vary Γ until $S_{\rm OCP}^{\rm MHNC}(q;\Gamma)$ mimics closely $S_{\phi}^{\rm MHNC}(q;\eta)$ (see, for example, Fig. 4 for the case of liquid sodium). It is interesting to note that the corresponding $-s_{\rm OCP}^{\rm ex}$ is found to be -4.13, which is deteriorated but comparable to the $s_{\rm MHNC}^{\rm ex}$ given in Table I. In view of the above comparison, it would be interesting if the present VMHNC theory can be reformulated to impose the additional thermodynamic self-consistency for the compressibility equation of state. Such a calculation, if feasible, will surely enrich our understanding of the structure and thermodynamics of liquid metals.

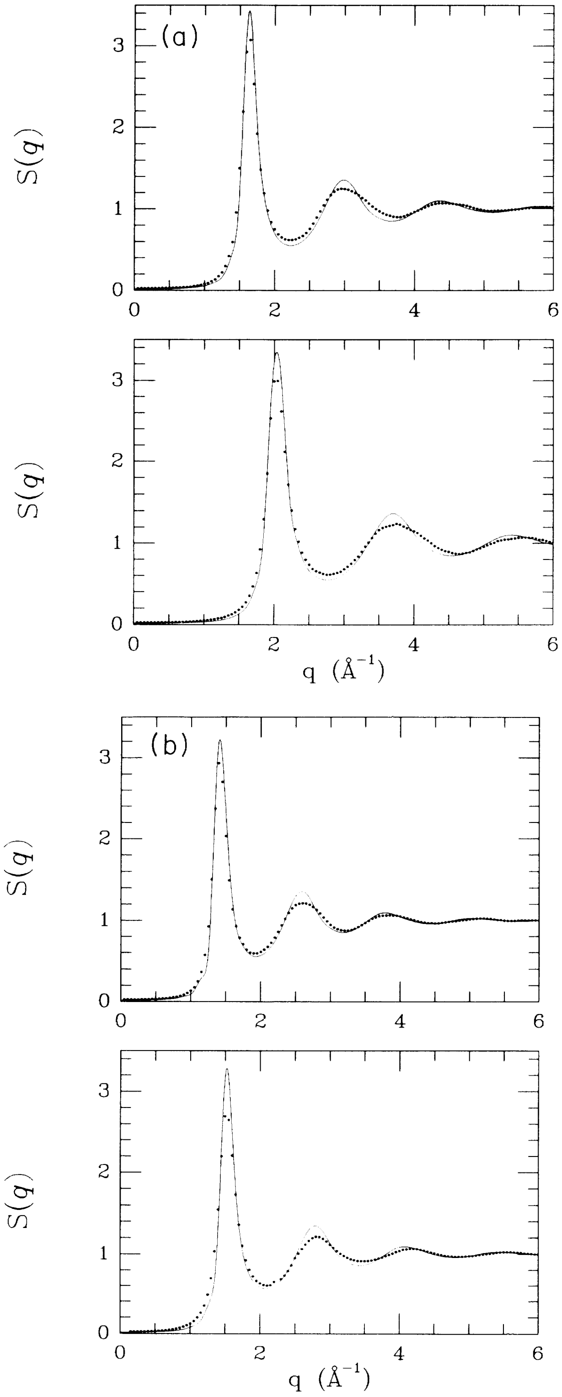

FIG. 3. (a) Static liquid-structure factor $S(q)$ for liquid K (top) and Na (bottom) metals at or near freezing calculated by Fourier-transforming the MHNC $g(r)$ [from Eq. (23) with $\delta_{\rm HS\text{-}PYHS}(\eta)$] and compared with observed data from Ref. [44] (denoted by solid circles). (b) Same as (a) but for liquid Cs (top) and Rb (bottom) metals. Notations of the curves are the same as in (a).

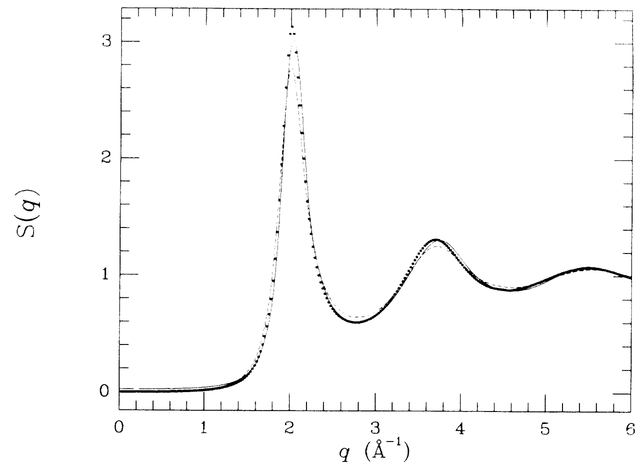

FIG. 4. Static liquid-structure factor $S(q)$ (solid curve) for liquid sodium at freezing calculated by Fourier-transforming the MHNC $g(r)$ [from Eq. (23)] compared with the "best" $S_{\rm OCP}^{\rm MHNC}$ $(q;\Gamma=175)$ (solid circles). The $S_{\rm OCP}^{\rm MHNC}$ $(q;\Gamma=141)$ (dashed curve) given in Table I is included also for comparison.

IV. CONCLUSION

The possibility of using the MHNC approach to structure and thermodynamic studies has been examined. Following the work of Rosenfeld [17,18], we reconsider

Lado's criterion to obtain the bridge parameter within the context of the Percus-Yevick hard-sphere approximation in some detail. We showed explicitly that the usual Lado's criterion [devoid of $\delta_{\text{HS-PYHS}}(\eta)$ in Eq. (23)], which takes advantage of the analytical simplicity of $B_{\text{PYHS}}(r;\eta)$, is inadequate for yielding an accurate $g^{\text{MHNC}}_{\phi,\text{PYHS}}(r;\eta)$. A correction to the usual Lado's criterion is demonstrated here to be necessary, and when this is done, a very accurate $g^{\text{MHNC}}_{\phi,\text{PYHS}}(r;\eta)$ is predicted. Calculated thermodynamic functions which emerge naturally in the theoretical framework provide insight to further calculations. The latter results reinforce our belief once more for the need of considering thermodynamic self-consistency for the reference system before it is implemented to the Gibbs-Bogoliubov inequality as stressed by us in a recent paper [1].

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APPENDIX: GIBBS-BOGOLIUBOV INEQUALITY IN MHNC THEORY

Starting from Eq. (5), the excess entropy per particle, $s^{\text{ex}}_{\text{MHNC}}=-S^{\text{ex}}_{\text{MHNC}}/Nk_B\geq 0$, can be written in MHNC theory for a HS bridge function as [17]

$$\begin{aligned}s^{\text{ex}}_{\text{MHNC}}={}&\tfrac{1}{2}\rho\int d\mathbf{r}\,g^{\text{MHNC}}_{\phi}(r;\eta)B_{\text{HS}}(r;\eta)\\&-\tfrac{1}{2}\rho\int d\mathbf{r}\{\tfrac{1}{2}[h^{\text{MHNC}}_{\phi}(r;\eta)]^2+h^{\text{MHNC}}_{\phi}(r;\eta)-g^{\text{MHNC}}_{\phi}(r;\eta)\ln g^{\text{MHNC}}_{\phi}(r;\eta)\}\\&-\frac{1}{2\rho}\frac{1}{(2\pi)^3}\int d\mathbf{k}\{\ln[1+\rho\tilde{h}^{\text{MHNC}}_{\phi}(k;\eta)]-\rho\tilde{h}^{\text{MHNC}}_{\phi}(k;\eta)\}-\tfrac{1}{2}\rho\int_0^{\eta}d\eta'\int d\mathbf{r}\,g^{\text{MHNC}}_{\phi}(r;\eta')\frac{\partial B_{\text{HS}}(r;\eta')}{\partial\eta'}\ .\end{aligned}\tag{A1}$$

The first three terms on the right-hand side of $s^{\text{ex}}_{\text{MHNC}}$ can be combined with the second term on the right-hand side of Eq. (5):

$$\beta\langle H_{\text{true}}\rangle_{\text{MHNC}}=\tfrac{1}{2}\rho\beta\int d\mathbf{r}\,g^{\text{MHNC}}_{\phi}(r;\eta)\phi(r)\ ,\tag{A2}$$

leading to $f^{\text{MHNC}}_{\phi}(\eta)$. The remaining term, upon consulting Eqs. (12) and (14) and then adding up, gives

$$\begin{aligned}s^{\text{ex}}_{\text{MHNC}}+\beta\langle H_{\text{true}}\rangle_{\text{MHNC}}&=f^{\text{MHNC}}_{\phi}(\eta)-\tfrac{1}{2}\rho\int_0^{\eta}d\eta'\int d\mathbf{r}\,g^{\text{MHNC}}_{\phi}(r;\eta')\frac{\partial B_{\text{HS}}(r;\eta')}{\partial\eta'}\\&=\mathcal{F}^{\text{VMHNC}}_{\phi}(\eta)\ .\end{aligned}\tag{A3}$$

Apart from the structure-independent energy terms, Eq (A3) is the same as the present Lado's criterion upon minimization of $\mathcal{F}^{\text{VMHNC}}_{\phi}(\eta)$ with respect to η.

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