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Equilibrium properties of liquids by the self-consistent-field method

Narinder K. Ailawadi and Ravinder Bansal
Institut für Theoretische Physik, Freie Universität Berlin, 1 Berlin 33, West Germany

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The modified self-consistent scheme of Singwi *et al.* (STLS) for the calculation of static structure of classical liquids is used to calculate equilibrium properties of liquid sodium and rubidium. First, the effect of the attractive part of the potential on the static structure factor is studied. Using the theoretical results for pair correlation function $g(r)$ we compute internal energy, pressure equation of state, high-frequency shear and bulk moduli, Einstein-frequency and second-frequency moments of the longitudinal- and transverse-current correlation functions. The corresponding expressions are also calculated by using the experimental $g(r)$ for liquid sodium and molecular-dynamics data for liquid rubidium. These results agree reasonably well with the theoretical predictions of the modified STLS theory. Disagreement in pressure and bulk modulus is due to the fact that the theory yields too high a compressibility.

I. INTRODUCTION

This paper is the third one in the series, and our aim has been to try to understand the equilibrium and dynamic properties of liquids within one single framework. In the first paper,[1] hereafter referred to as I, the theory[2] of Singwi *et al.* (STLS) for calculating the density response function of an interacting electron gas was modified to take into account the fact that the pair correlation function $g(r)$ vanishes in the highly repulsive hard-core region of the pair potential for classical liquids. This modified self-consistent iterative scheme was applied to calculate the static structure factor $S(q)$ of liquid sodium and rubidium. The calculated results for both these metals were found to be in good agreement with the observed data[3,4] and were somewhat better than the predictions of Weeks, Chandler, and Andersen's (WCA) theory.[5] In the second paper,[6] we analyzed the behavior of the density-fluctuation spectrum $S(q,\omega)$ in liquid rubidium using the modified STLS scheme discussed in I. Based on the physical argument that for a strongly interacting system, such as a liquid, there is still a residual interaction left even after collective effects are taken into account, it was proposed that the free-particle response function appearing in the STLS theory (as well as its modified form) should be replaced by the response function corresponding to self-motion of the atoms. It was found that the numerical predictions of the theory for $S(q,\omega)$ are in overall good agreement with the data[7] for momentum transfers $q \geqslant 1.5$ Å^{-1}.

The aim of the present paper is to investigate the extent of the agreement between equilibrium properties calculated using the static structure data obtained in I and the experimental values. These properties include internal energy, pressure equation of state, instantaneous elastic moduli, and second-frequency-moment sum rules of both the longitudinal- and transverse-current correlation functions in liquids. All these quantities are expressible in terms of integrals involving the products of $g(r)$ and appropriate derivatives of the pair potential $\phi(r)$. In addition, we also investigate the characteristic effects of the repulsive and attractive parts of the potential on the liquid structure.

II. THEORY

A. Modified STLS scheme

The dynamical density response function in the STLS[2] theory is given by

$$\chi(q,\omega)=\chi_0(q,\omega)/[1-\Psi(q)\chi_0(q,\omega)]\,, \tag{1}$$

where $\chi_0(q,\omega)$ is the dynamical density response function of a free-particle system and $\Psi(q)$ is the Fourier-transform of the polarization potential $\Psi(r)$, defined by

$$\frac{d\Psi(r)}{dr}=g(r)\,\frac{d\phi(r)}{dr}\,. \tag{2}$$

Using the Kramers-Kronig relation and fluctuation-dissipation theorem, which relates the dynamical structure factor $S(q,\omega)$ to the imaginary part of the density response function, it can be shown that

$$S(q)=1/[1+n\Psi(q)/k_BT]\,. \tag{3}$$

The symbols n, k_B, and T have their usual meanings. Note that the polarization potential is formally related to the direct correlation function $c(r)$ through the relation

$$\Psi(r)=-k_BTc(r)\,. \tag{4}$$

Given a pair potential, the effective mean field $\Psi(q)$ can, in principle, be determined by solving Eqs. (2) and (3) in a self-consistent manner. However, such an iterative procedure for simple liquids leads to computational difficulties because of the highly repulsive nature of the pair potential in the hard-core region. To overcome this difficulty, it is assumed in I that

$$\frac{d\Psi(r)}{dr} = g(r)\,\frac{d\phi(r)}{dr} \quad \text{for } r > r_0 , \tag{5}$$

where r_0 is roughly the hard-core diameter and

$$\Psi(r) = a + b\left(1 - \frac{r}{r_0}\right) + \left(1 - \frac{r}{r_0}\right)^2 \times \sum_{n=0}^{\infty} c_n P_n\left(\frac{2r}{r_0} - 1\right) , \quad r < r_0 \tag{6}$$

where the P_n's are the Legendre polynomials. The coefficients a and b are fixed by demanding that $\Psi(r)$ be continuous at $r = r_0$. The parameters c_n are determined by minimization of a functional of the form

$$\mathcal{I}(\Psi) = \int d\vec{r}\,[1 - g(r)]\,\Psi(r) - [n^2(2\pi)^3]^{-1}k_BT \times \int d\vec{q}\left[\frac{n\Psi(q)}{k_BT} - \ln\left(1 + \frac{n\Psi(q)}{k_BT}\right)\right] , \tag{7}$$

where the functional $\mathcal{I}(\Psi)$ plays the role of Helmholtz free energy. For more details, the reader is referred to paper I.

B. Equilibrium quantities

We now write the expressions for various equilibrium quantities which we compute using the results for $g(r)$ obtained in I. The first one is the internal energy,

$$E = \tfrac{3}{2}k_BT + \tfrac{1}{2}n\int d\vec{r}\,g(r)\phi(r) . \tag{8}$$

The second is the pressure equation of state,

$$\frac{P}{nk_BT} = 1 - \frac{n}{6k_BT}\int d\vec{r}\,r\,g(r)\,\frac{d\phi(r)}{dr} . \tag{9}$$

Both Eqs. (8) and (9) can be derived by standard statistical mechanics, once the interatomic potential is known. Other quantities are the high-frequency bulk and shear moduli B and G, respectively. Zwanzig and Mountain[8] have shown that in simple liquids these moduli can be expressed in terms of the static pair correlation function and the pair potential,

$$B = \tfrac{2}{3}nk_BT + P + \tfrac{2}{9}\pi n^2 \int_0^\infty dr\,g(r)r^3\frac{d}{dr}\left(r\,\frac{d\phi(r)}{dr}\right) , \tag{10}$$

$$G = nk_BT + \tfrac{2}{15}\pi n^2 \int_0^\infty dr\,g(r)\,\frac{d}{dr}\left(r^4\,\frac{d\phi(r)}{dr}\right) . \tag{11}$$

These generalized elastic moduli are further related to the long-wavelength limits of the second frequency moments of the spectral function of the longitudinal- and transverse-current correlation functions in liquids,

$$G = mn\lim_{q\to 0}\frac{\omega_t^2(q)}{q^2} , \quad \tfrac{4}{3}G + B = mn\lim_{q\to 0}\frac{\omega_l^2(q)}{q^2} , \tag{12}$$

where

$$\langle\omega_l^2\rangle = \omega_l^2(q) = \frac{3q^2k_BT}{m} + \frac{n}{m}\int d\vec{r}\,g(r)(1 - \cos qx)\,\frac{\partial^2\phi(r)}{\partial x^2} \tag{13}$$

and

$$\langle\omega_t^2\rangle = \omega_t^2(q) = \frac{q^2k_BT}{m} + \frac{n}{m}\int d\vec{r}\,g(r)(1 - \cos qx)\,\frac{\partial^2\phi(r)}{\partial y^2} . \tag{14}$$

Another quantity of interest is the Einstein frequency

$$\Omega_E^2 = \frac{n}{m}\int d\vec{r}\,g(r)\,\frac{\partial^2\phi(r)}{\partial x^2} , \tag{15}$$

which is quite generally used in the theory of dynamics of liquids.

III. RESULTS

We now describe the results of the modified STLS theory for liquid sodium at temperature 473 °K and density 0.904 g cm^{-3}. The potential of Shyu *et al.*[9] was used as input for liquid sodium and that of Price *et al.*[10] for liquid rubidium ($T = 319\,^\circ$K, $\rho = 1.502$ g cm^{-3}). Liquid rubidium may be considered to be a test of the theory because our results are compared with molecular-dynamics calculations of Rahman,[4] which were carried out using the potential of Price *et al.*[10] as input.

Starting with an approximate input set of parameters c_n and a given value of $g(r)$, the iterative procedure consists of calculating $\Psi(r)$ in the region $r > r_0$ from Eq. (5) and $\Psi(r)$ in the small-r region, $r < r_0$, from Eq. (6) and substituting in Eq. (3) to get $S(q)$. This $S(q)$ and its smoothed Fourier transform $g(r)$ is substituted in Eq. (7) and the new values of the parameters c_n are calculated from

$$\frac{\partial\mathcal{I}}{\partial c_n} = 0, \quad n = 0, 1, 2, \ldots \tag{16}$$

which correspond to the condition that the functional $\mathcal{I}(\Psi)$ given by Eq. (7) is minimized. With this new set, and the new input $g(r)$ obtained from

TABLE I. Equilibrium properties of liquid rubidium and sodium.[a]

	$g(r)$ taken from	E/k_BT	P/nk_BT	B/nk_BT	G/nk_BT	$(\frac{4}{3}G+B)/nk_BT$	$\Omega_{E}\tau$
Rubidium	Theory	−3.9936	3.2055	44.1396	23.8371	75.9225	12.7210
	Molecular dynamics[b]	−3.5209	5.9546	51.4851	24.9455	84.7459	13.5418
Sodium	Theory	−1.9785	1.3288	8.5459	4.7390	14.8645	15.8836
	Experiment[c]	−1.8204	2.3643	10.7311	4.8015	17.1332	16.9890

[a] The results for liquid rubidium correspond to a cutoff $r_c = 11.9594$ Å and for sodium $r_c = 18$ Å.

[b] Reference 4.

[c] Reference 3.

$$g_{n+1}^{\text{in}}(r) = (1-\gamma)\,g_{n-1}^{\text{in}}(r) + \gamma g_n^{\text{out}}(r), \quad 0<\gamma<1 \qquad (17)$$

the procedure is repeated until the self-consistency is achieved.

In order to study first the effect of the attractive part of the potential on the equilibrium structure, we use the parameters c_n tabulated in Table I of I for liquid Na and assume $\phi(r)$ to be zero for $r > r_0$ ($r_0 = 2.858$ Å) and calculate $\Psi(r)$ and $S(q)$ from Eqs. (6) and (3). These results are shown in Figs. 1 and 2 by dashed curves. Now using the given $\phi(r)$ for $r > r_0$, $\Psi(r)$ is calculated from Eqs. (5) and (6) and $S(q)$ from Eq. (3). These results are plotted in Figs. 1 and 2 as solid lines and show that marked differences arise when only the expression (6) for $\phi(r)$ in the region $r < r_0$ is used to calculate $S(q)$. The peak heights and peak positions as well as the small-q behavior of $S(q)$ change significantly by the inclusion of the full potential. The same holds for the pair correlation function $g(r)$ (see Fig. 3).

Using the theoretical results for $g(r)$ from I and the potential of Ref. 10 for liquid rubidium as in-

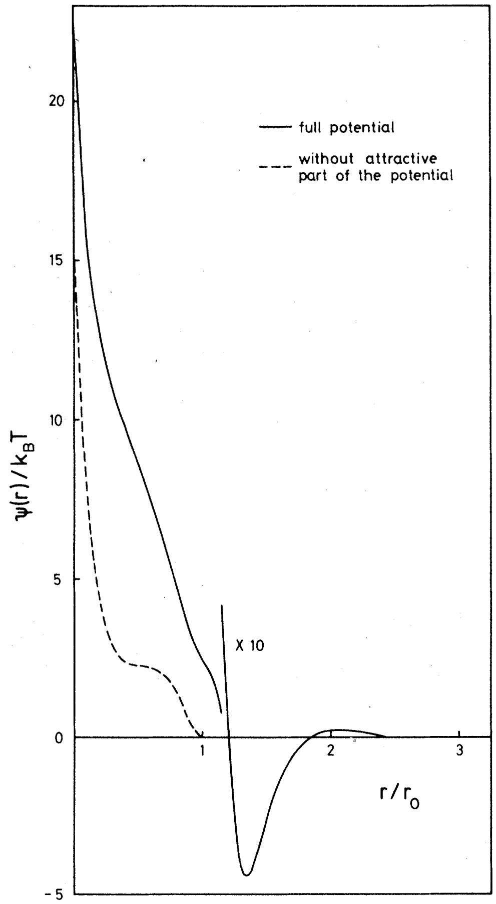

FIG. 1. Effective potential $\Psi(r)$ vs r/r_0 for liquid sodium. $r_0 = 2.858$ Å.

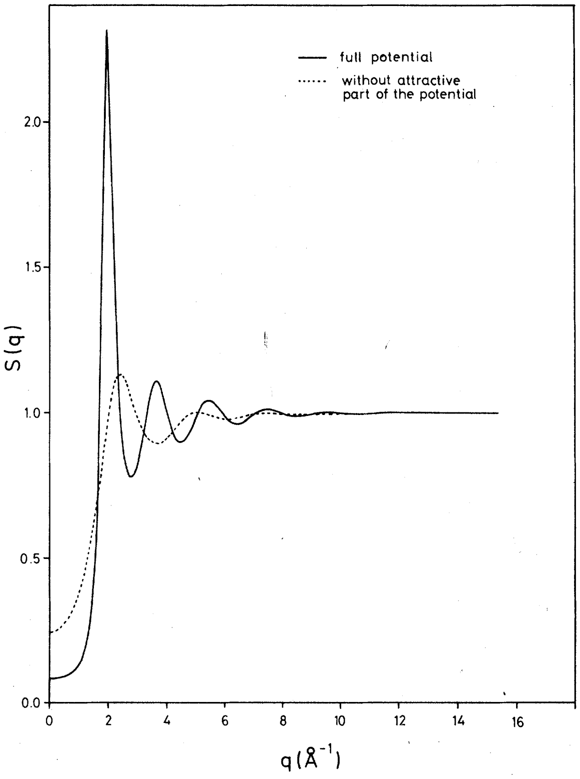

FIG. 2. Static structure factor $S(q)$ vs q for liquid sodium.

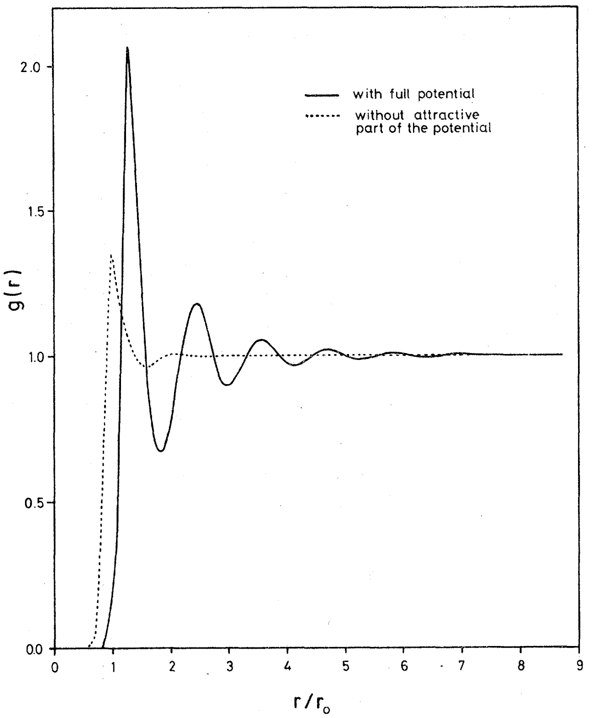

FIG. 3. Static pair correlation function $g(r)$ vs r/r_0.

put, we compute internal energy, pressure, the high-frequency bulk and shear elastic moduli B and G from Eqs. (8)–(11), and the Einstein frequency Ω_E. These are listed in Table I and are compared with the corresponding results obtained by using Rahman's molecular-dynamics data for $g(r)$. Similar results for liquid sodium are also presented in Table I, but in this case we compare our results with those obtained using the experimental data[3] for $g(r)$ together with the Shyu *et al.* potential. The theoretical results agree quite well with those obtained from experimental and molecular-dynamics data. Furthermore, the generalized Cauchy identity $B=\frac{5}{3}G+2(P-nk_BT)$ is satisfied by our theoretical results. The only exception seems to be the pressure, which shows disagreement with the data in both cases (Rb and Na). The cause of this discrepancy is discussed in Sec. IV.

In Fig. 4, the wave-number dependence of the quantities $\omega_l(q)$ and $\omega_t(q)$, defined through Eqs. (13) and (14), is plotted for the case of liquid rubidium. Again theoretical results are compared with the ones obtained using molecular-dynamics data for $g(r)$. Figure 5 shows the analogous curves for liquid sodium, and the results are compared with those obtained by using the x-ray-diffraction data for $g(r)$ of Greenfield *et al.*[3] The agreement in both cases is clear. Note that the slopes of $\omega_l(q)$ and $\omega_t(q)$ curves (in both Figs. 4 and 5) in the small-q region yield the elastic moduli and agree with the ones presented in Table I. Furthermore, for intermediate values of q, oscillations in the $\omega_l(q)$ curve (see Fig. 4) correspond to peaks in $S(q)$. Note that the characteristic dip in the $\omega_l(q)$ curve for liquid sodium is almost absent. This difference in the behavior of $\omega_l(q)$ is due to the fact that rubidium is being studied near its melting temperature and therefore has more structure as compared to sodium studied at 100°K above its melting temperature. Recent measurements on liquid rubidium and Sn have shown that the peak height of $S(q)$ decreases with increasing temperature.[11,12]

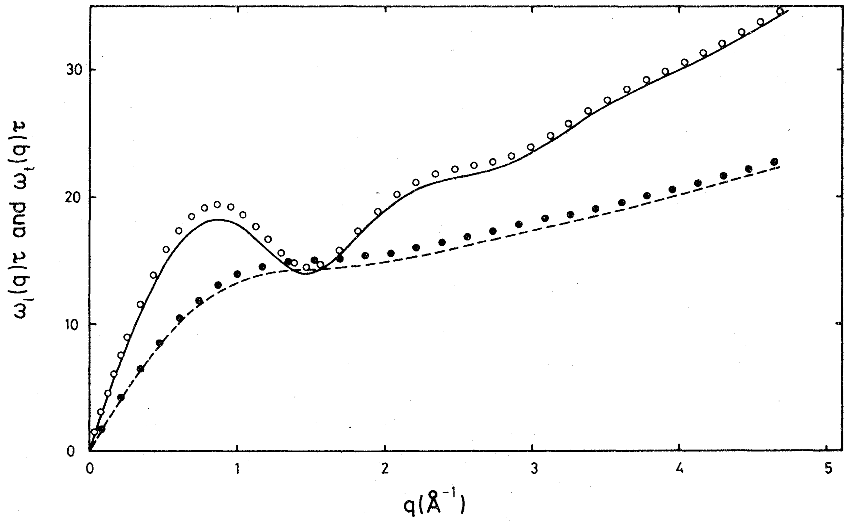

FIG. 4. $\omega_l(q)\tau$ and $\omega_t(q)\tau$ vs q for liquid rubidium. Full curve and open circles: $\omega_l(q)\tau$ calculated using theoretical and molecular-dynamics data for $g(r)$. Dashed curve and closed circles: $\omega_t(q)\tau$ calculated using theoretical and molecular-dynamics data for $g(r)$. $\tau=2.2257\times10^{-12}$ sec.

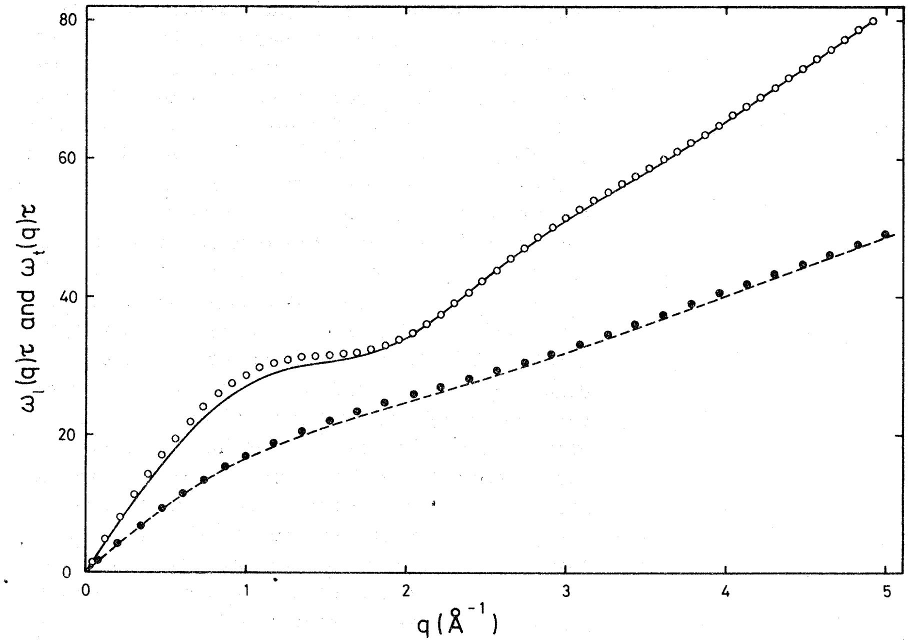

FIG. 5. $\omega_l(q)\tau$ and $\omega_t(q)\tau$ vs q for liquid sodium. Full curve and open circles: $\omega_l(q)\tau$ calculated using theoretical and x-ray-diffraction data for $g(r)$. Dashed curve and closed circles: $\omega_t(q)\tau$ calculated using theoretical and x-ray-diffraction data for $g(r)$. $\tau = 2.2257 \times 70^{-12}$ sec.

IV. DISCUSSION

We studied the effect of the pair potential $\phi(r)$ for $r > r_0$ (loosely called the attractive part) on the equilibrium structure of liquid sodium and find that the $r > r_0$ part of $\phi(r)$ plays an important role in determining $S(q)$. However, in our calculations, the $r < r_0$ part of the potential does not include the full repulsive part of the potential as discussed in the WCA papers.[5] On the other hand, the hard-core part of $\phi(r)$ is included, and hence we can safely make the statement that the attractive part of the potential is essential in the modified STLS theory to get the correct $S(q)$.

In order to study the usefulness of the theory, we calculate various equilibrium properties of liquid sodium and rubidium using first the theoretically calculated pair correlation function $g(r)$. These results are compared with molecular dynamics for liquid rubidium by substituting the $g(r)$ data obtained by Rahman. For liquid sodium, these calculations are repeated using the experimental data for $g(r)$ keeping the same potential of Shyu *et al.* Except for the pressure equation of state, the theoretical results are in reasonably good agreement with the molecular-dynamics results for liquid rubidium and experimental results for liquid sodium.

This discrepancy becomes clear when the pressure Eq. (9) is examined more carefully. Using Eq. (4), Eq. (9) can be expressed as

$$\frac{P}{nk_BT} = 1 - \tfrac{1}{2}n \int d\vec{r}\, c(r)\,, \qquad (18)$$

which reduces to

$$P = \tfrac{1}{2}n\left[k_BT + \left(\frac{\partial P}{\partial n}\right)_{T,V}\right]. \qquad (19)$$

It is well known that the STLS theory yields almost twice the correct isothermal compressibility $\chi_T = (1/n)(\partial n/\partial P)_{T,V}$, as shown, for example, in Fig. 2. Thus, it is clear that resulting pressure would be small in this theory. For the same reason, the generalized Cauchy identity yields a lower value of the bulk modulus B.

Furthermore, frequency moments $\omega_l^2(q)$ and $\omega_t^2(q)$ defined by Eqs. (13) and (14) are reproduced quite well by using the theoretical $g(r)$ and can be used to provide a check on any theory of collective excitations in liquids. Recently, Block[12] considerably simplified the numerical technique used to determine the coefficients c_n, $n = 0, 1, 2, \ldots$ in Eq. (6). Instead of Eq. (16), he uses Eq. (7) directly and applies a three-point parabolic fit to compute the new values of the parameters c_n. In this way, he obtains very good fit to the $S(q)$ data for *nine* different temperatures in the range 450–1400 °K for q up to 2.5 Å^{-1}.

Finally, we would like to point out that only ion contribution to the thermodynamic quantities corresponding to pairwise interaction has been studied. In order to compare with the laboratory experimental data, one must add volume-dependent terms corresponding to the electronic and band-structure contribution as shown by Price[10] for liquid sodium.

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