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Optimized random-phase approximation for the structure of expanded fluid rubidium

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The liquid-structure factors of fluid rubidium are calculated for a series of states along the saturated-vapor-pressure curve, ranging from temperatures close to the melting point up to the critical point. The calculation is based on the optimized random-phase approximation and on effective interatomic pair potentials derived from pseudopotential perturbation theory. The results are compared with the static-structure factors measured using elastic neutron scattering. Good agreement is found for temperatures up to $T=1400$ K. From the divergence of $S(0)$ the critical temperature is calculated to be $T_c=2120\pm5$ K, compared with an experimental value of $T_c=2090\pm20$ K. The calculation reproduces the strong increase of the long-wavelength scattering, but we find it to be confined to a narrower temperature interval below T_c. We bring evidence that this is due to the breakdown of the nearly-free-electron approximation in a regime where the mean free path of the electrons becomes smaller than the average interatomic distance.

I. INTRODUCTION

For the fluid alkali metals, characteristic changes of the scattering behavior and of the microscopic structure as functions of temperature and density approximating the critical point have been observed experimentally.[1,2]

Theoretically the thermodynamic and structural properties of the liquid alkali metals at high densities are now quite well understood. Computer simulations[3–6] have undoubtedly confirmed the concept of density-dependent effective interatomic pair potentials. Thermodynamic perturbation calculations[7–9] have elucidated the influence of the repulsive and attractive interactions on the microscopic structure of the liquid metals. For high densities near the melting point, the physical picture emerging from these theories is that the liquid metal has its volume determined by the volume energy and by the attractive part of the interatomic potential, but once the volume has been determined, the liquid metal may be considered as a hard-sphere fluid confined within that volume. For the heavy alkali metals, the repulsive part of the interatomic interaction is extremely soft and Kumaravadivel and Evans[9] have shown that the Weeks-Chandler-Andersen (WCA) functional expansion[10,11] may be used to correct the hard-sphere description for the softness of the interatomic repulsions. However, a critical evaluation of their results shows that although the functional expansion[10,11] provides the necessary damping of the strong oscillations in the hard-sphere structure factor at larger momentum transfers, it does not eliminate the phase difference relative to the static-structure factor generated by a computer simulation. Tentatively, this phase difference may be considered as an effect of the attractive interactions.

Only a few attempts have been made to study the structure of expanded liquid metals theoretically. Only Mountain[12] and Tanaka[13] presented the results of computer simulations. Mountain found only a rather moderate agreement of his Monte Carlo study based on the interatomic potentials of Price[14] with the experimental data available at that time,[15] but in fact the agreement with the more recent and more accurate experimental data[1] is really good, except for the long-wavelength regime at the highest temperature studied ($T=1400$ K). Tanaka[13] performed molecular-dynamics calculations (based on slightly different potentials) close to the saturated-vapor-pressure curve including the critical point. Again one finds good agreement with experiment for moderate temperatures and momentum transfers larger than 0.5 a.u., but the long-wavelength density fluctuations are definitely not adequately reproduced.

This is the motivation for performing another theoretical investigation of the structure of expanded fluid rubidium, which is based on liquid state theory rather than on computer simulation. Evidently what is needed is a theory to describe the influence of the attractive forces which should supplement the already existing theories for the effect of the repulsions. Andersen and Chandler[16,17] and Andersen *et al.*[18] have proposed a series of related perturbation approximations for calculating the effect of attractive interactions which they call the optimized random-phase approximation (ORPA) and the optimized cluster theory (OCT). Their theory may be cast into the form of a variational problem defining a renormalized ("optimized") potential for the attractive forces. This is a very attractive feature if systems with rather complicated pair potentials—such as liquid metals—are to be considered.

We show that already at high densities and temperatures close to the melting point the attractive forces are crucial for an exact description of the liquid structure. Compared to a system with repulsive interactions only, the effect of the attractive interaction is to sharpen the first peak and to shift the position of the second peak to slightly smaller momentum transfers—we find that this is just what is needed to get good agreement. A consideration of the changes in the pair-correlation function induced by the attractive potential allows us to establish the importance of the oscillatory part of the potential. These effects are found to persist at higher temperatures, but in addition we find that the onset of the long-wavelength density fluctuations is triggered mainly by the strength of the attractive interactions. Up to $T=1400$–1600 K the agreement between theory and experiment is good. At higher temperatures the theory underestimates the strong increase in the long-wavelength scattering. This may have different reasons: one point is that our calculation yields a critical temperature of about $T_c \simeq 2120 \pm 5$ K whereas experimentally one finds $T_c = 2090 \pm 20$ K. For a calculation of the critical temperature this is certainly as good an agreement as can be expected, but of course this means that the onset of the long-wavelength density fluctuations is shifted to higher temperatures. Still, even if we plot $S(0)$ against $t=T/T_c$, we find that, experimentally, the increase in the low-q scattering develops already at lower values of t than predicted by our calculation. In this respect an analysis of the electronic transport properties is interesting: We find that at temperatures $T \geq 1600$ K the electronic mean free path is already smaller than the mean interatomic distance. This means that the linear-response theory used for the construction of the potential has to be modified. Another important point is the magnetic anomalies observed at these temperatures[19]—their description again requires a modification of the electronic response function (spin-polarized response). This, however, can only be a subject of future research.

II. INTERATOMIC POTENTIALS

In the linear screening approximation the effective interatomic pair potential in a metal consists of the direct Coulomb repulsion between the ions, plus the attraction of the first ion to the screening charge distribution induced by the pseudopotential of the second ion[20]

$$V(r,\rho)=\frac{Z^2e^2}{r}+\int\int V_{\text{ion}}(\vec{r}\,'')\chi(\vec{r}\,''-\vec{r}\,',\rho)\times V_{\text{ion}}^{\text{sc}}(\vec{r}\,'-\vec{r})d\vec{r}\,'d\vec{r}\,'' \,, \tag{1}$$

where $\chi(\vec{r},\rho)$ is the dielectric susceptibility of the interacting electron gas, and $V_{\text{ion}}(\vec{r})$ and $V_{\text{ion}}^{\text{sc}}(\vec{r})$ are the bare and screened ionic pseudopotentials. In practice, $V(r,\rho)$ is calculated by Fourier transforming the reciprocal space expression

$$\hat{V}(q,\rho)=\frac{4\pi Z^2e^2}{\Omega q^2}+F(q) \,, \tag{2}$$

$$V(r,\rho)=\frac{Z^2e^2}{r}+\frac{\Omega}{2\pi^2 r}\int_0^\infty F(q)\sin(qr)q\,dq \,, \tag{3}$$

with the energy wave number characteristic $F(q)$ (assuming a local pseudopotential)

$$F(q)=\frac{\Omega}{2}\frac{\hat{\chi}(q)}{\hat{\epsilon}(q)}\,|\hat{V}_{\text{ion}}(q)|^2 \,, \tag{4}$$

where Ω is the atomic volume, Z the valence, and $\hat{\epsilon}(q)$ is the dielectric function

$$\hat{\epsilon}(q)=1-\frac{4\pi e^2}{q^2}[1-G(q)]\hat{\chi}(q) \,, \tag{5}$$

where $G(q)$ is the local field factor correcting for exchange and correlation interactions between the electrons. The effective pair potential depends on the electron density ρ through the density dependence of $\hat{\chi}(q)$ and $\hat{\epsilon}(q)$ and a possible slight density dependence of the bare pseudopotentials, but it is the density dependence of the screening functions which gives the dominant effect.[21] Hence, in order to simplify the calculations we approximate the ionic pseudopotential by a simple local empty-core model[22] with the core radius r_c fixed at the value $r_c=2.47$ a.u. which minimizes the total energy of crystalline rubidium at the observed density. Our value of r_c is very close to that of $r_c=2.40$ a.u. used by Price[23] in a series of calculations of the properties of crystalline and liquid rubidium. On the other hand, we have been very careful in the choice of an appropriate form of the local field factor $G(q)$. The apparently very drastic effects of different possible approximations to $G(q)$ on $V(r,\rho)$ have been widely discussed (see, e.g., Ref. 24). What has been often overlooked is that the dielectric function of the strongly coupled degenerate electron gas has to satisfy a number of consistency relations relating $G(q)$ to the correlation energy, to the compressibility of the electron gas, to the electron-electron pair-correlation function, etc. In our case the consistency relations have to be satisfied over an extremely wide range of electronic densities ($r_s=5$–9 a.u.). After eliminating all approximations which violate one or more of these requirements, we are left with only a very few options which all produce very similar pair potentials. The dielectric function of Ichimaru and Utsumi[25,26] used in this work represents in our view an optimum compromise between accuracy and computational simplicity. Let us note that the aforementioned computer simulations of liquid rubidium[4,5,12,13] are all based on an early version of the local field factor $G(q)$ due to Singwi *et al.*[27] which violates the consistency rules, especially at low electron densities.

In the following we will have to split the pair potential into a purely repulsive short-range interaction $V_0(r)$ and the remaining essentially attractive long-range interaction $V_1(r)$. We do this by following the WCA convention which places the division at the first minimum situated at r_0 [$V(r_0)=V_{\min}$] and write

$$V(r)=V_0(r)+V_1(r) \tag{6}$$

with

$$V_0(r)=\begin{cases}V(r)-V_{\min}, & r<r_0\\ 0, & r>r_0\end{cases} \tag{7}$$

and

$$V_1(r)=\begin{cases}V_{\min}, & r<r_0\\ V(r), & r>r_0 \,.\end{cases} \tag{8}$$

In the calculations we will need the Fourier transform

$\hat{V}_1(q)$ of the attractive interactions, but one should avoid the numerical inaccuracies associated with a double Fourier transform: first $\hat{V}(q)$ to get $V(r)$ and then $V_1(r)$ to get $\hat{V}_1(q)$. We follow McLaughlin and Young[28] in writing

$$\hat{V}_1(q)=\frac{4\pi}{q}\int_0^\infty [V(r)\Theta(r-r_c)-V_{\min}]\sin(qr)r\,dr \tag{9}$$

and, after inserting (3) into (9) and changing the sequence of integrations, we find

$$\begin{aligned}\hat{V}_1(q)={}&\frac{4\pi}{q^3}[\sin(qr_0)-qr_0\cos(qr_0)]V_{\min}\\&-\frac{2}{\pi q}\int_0^\infty F(q')\left[\frac{\sin[(q-q')r_0]}{q-q'}-\frac{\sin[(q+q')r_0]}{q+q'}\right]q'dq'+2F(q)+\frac{4\pi Z^2e^2}{\Omega q^2}\cos(qr_0)\end{aligned} \tag{10}$$

with the low-q limit given by

$$\begin{aligned}\hat{V}_1(0)={}&\frac{4\pi r_0^3}{3}V_{\min}\\&-\frac{2}{\pi}\int_0^\infty F(q')\frac{\sin(q'r_0)-q'r_0\cos(q'r_0)}{q'}dq'\\&-2\pi Z^2e^2r_0^2+\hat{V}(0)\;,\end{aligned} \tag{11}$$

$\hat{V}(0)$ being given by

$$\hat{V}(0)=4\pi^2Z^2e^2\left[r_c^2+\frac{\pi}{4k_F}-\frac{\gamma}{k_F^2}\right], \tag{12}$$

where

$$G(q)\rightarrow\gamma q^2/k_F^2\;\;(for\text{ small }q) \tag{13}$$

is the compressibility factor of the electron gas[25,26] and k_F is the Fermi momentum.

III. OPTIMIZED RANDOM-PHASE APPROXIMATION FOR CONTINUOUS POTENTIALS

In the following we recapitulate very briefly the application of the ORPA to systems with continuous potentials. The ORPA has been developed in a form specific to systems with hard-core interactions. For systems with continuous potentials we need a theory which allows us to describe the repulsive interactions in terms of effective hard-core potentials.

A. Repulsive interactions

The first step consists in replacing the soft repulsive interaction $V_0(r)$ by an effective hard-sphere interaction $V_\sigma(r)$ with diameter σ. This is achieved by expanding the free energy in terms of the function $B_\sigma(r)$ defined by[10,11]

$$B_\sigma(r)=y_\sigma(r)\{\exp[-\beta V_0(r)]-\exp[-\beta V_\sigma(r)]\} \tag{14}$$

with

$$y_\sigma(r)=\exp[\beta V_\sigma(r)]g_\sigma(r),\;\;\beta=1/k_BT\;. \tag{15}$$

$g_\sigma(r)$ is the hard-sphere pair-correlation function, which we describe by the analytical solution of the Percus-Yevick[29] equation. The hard-sphere diameter σ is determined at each temperature and density by the WCA requirement

$$\hat{B}_\sigma(q=0)=\int B_\sigma(r)d^3r=0 \tag{16}$$

which optimizes the convergence of the free-energy expansion. Finally, the pair-correlation function is shown[10,11] to be given by

$$\begin{aligned}g_0(r)&=g_\sigma(r)\exp[\beta V_\sigma(r)-\beta V_0(r)]\\&=y_\sigma(r)\exp[-\beta V_0(r)]\end{aligned} \tag{17}$$

and the corresponding static-structure factor $S_0(q)$ by

$$S_0(q)=S_\sigma(q)+\rho\hat{B}_\sigma(q) \tag{18}$$

where ρ is the number density. At high densities the static-structure factor $S_0(q)$ given by Eq. (18) has a small unphysical hump at small q (near $q\simeq\pi/\sigma$). Jacobs and Andersen[30] proposed on the basis of a diagrammatic expansion of the pair-correlation function to replace (18) by

$$S_0(q)=S_\sigma(q)[1-\rho S_\sigma(q)\hat{B}_\sigma(q)]^{-1} \tag{19}$$

and showed that this avoids the unphysical hump. Later Telo da Gama and Evans[31] rederived Eq. (19) using density-functional techniques and showed that it has essentially a low-q validity. In our calculations we found that the pair-correlation function $g_0(r)$ obtained by Fourier transforming (19) is unphysical at small distances [$g_0(r)\neq 0$ for $r\ll\sigma$], hence it is not a suitable basis for the application of the ORPA. Therefore we will use the original WCA equation (18). This is justified because we find that the WCA hump is very small at densities that are not too high [$\Omega>800$ (a.u.)^3].

B. Attractive interactions

The theory for the effect of the attractive interactions is based on the Ornstein-Zernike (OZ) equation[32] for the direct correlation function $c(r)$ which may be written either in configuration space

$$h(r_{12})=c(r_{12})+\rho\int c(r_{13})h(r_{32})d^3r_3\;, \tag{20}$$

or in Fourier space

$$\hat{h}(q)=\hat{c}(q)/[1-\rho\hat{c}(q)]\;, \tag{21}$$

where $h(r)=g(r)-1$ is the total correlation function [note $S(q)=1+\rho\hat{h}(q)$]. All the integral equations of the theory of liquids may be formulated as the OZ equation supplemented by a "closure relation" relating $c(r)$ and $h(r)$ to the interatomic potential $V(r)$. The closure relation defining the Percus-Yevick[29] equation is given by

$$c(r)=\{1-\exp[\beta V(r)]\}g(r) . \tag{22}$$

If we decompose the pair interaction according to Eq. (6), and replace the repulsive potential by the hard-sphere reference potential V_σ, this leads logically to a separation of the correlation functions into two terms

$$h(r)=h_\sigma(r)+\delta h(r) , \tag{23a}$$

$$c(r)=c_\sigma(r)+\delta c(r) . \tag{23b}$$

Since we know the solution of the OZ equation

$$h_\sigma(r_{12})=c_\sigma(r_{12})+\rho\int c_\sigma(r_{13})h_\sigma(r_{32})d^3r_3 \tag{24}$$

for the reference system, it is useful to subtract the purely repulsive couplings from both sides of Eq. (20) to give the OZ equation in a residual form

$$\begin{aligned}\delta h(r_{12})=\delta c(r_{12})&+\rho\int c_\sigma(r_{13})\delta h(r_{32})d^3r_3\\&+\rho\int \delta c(r_{13})h_\sigma(r_{32})d^3r_3\\&+\rho\int \delta c(r_{13})\delta h(r_{32})d^3r_3 ,\end{aligned} \tag{25}$$

or in Fourier space

$$\delta\hat{h}(q)=S_\sigma(q)\delta\hat{c}(q)S_\sigma(q)/[1-\rho\delta\hat{c}(q)S_\sigma(q)] . \tag{26}$$

The random-phase approximation (RPA) introduces the asymptotic form of the direct correlation function

$$c(r)=-\beta V(r) \tag{27}$$

as the closure condition. As the solution of $c_\sigma(r)$ is known, one assumes the RPA only for the residual part $\delta c(r)$,

$$\delta c(r)=-\beta V_1(r) . \tag{28}$$

The RPA in the form of Eq. (28) has the unphysical feature of a pair-correlation function which is nonzero inside the hard core. Andersen *et al.*[16–18] proposed to replace the RPA by the ORPA defined by [note $h_\sigma(r)=-1$ for $r<\sigma$]

$$\delta c(r)=-\beta V_1(r),\quad r>\sigma \tag{29a}$$

$$\delta h(r)=0,\quad r<\sigma \tag{29b}$$

or equivalently

$$\delta c(r)=-\beta V_1(r),\quad r>\sigma \tag{30a}$$

$$\delta c(r)=-\beta\phi(r),\quad r<\sigma \tag{30b}$$

where the optimized potential $\phi(r)$ ($r<\sigma$) is determined such that Eq. (29b) is satisfied. Equations (29) or (30) define the closure relation to the residual OZ equation [Eqs. (25) and (26)]. This integral equation may be solved using a variational procedure. Define the functional F by

$$\begin{aligned}F(\delta\hat{c})=\frac{1}{(2\pi^3)\rho}\int d^3q\{&\rho S_0(q)\delta\hat{c}(q)\\&+\ln[1-\rho S_0(q)\delta\hat{c}(q)]\}\end{aligned} \tag{31}$$

and take its functional derivative with respect to $\delta\hat{c}(q)$

$$\frac{\delta F(\delta\hat{c})}{\delta[\delta\hat{c}(q)]}=-\frac{\rho}{(2\pi)^3}\delta\hat{h}(q) . \tag{32}$$

After Fourier transforming we have

$$\frac{\delta F(\delta c)}{\delta[\delta c(r)]}=-\rho\,\delta h(r) . \tag{33}$$

Combined with Eqs. (29b) and (30b) we find that the correct behavior of the optimized potential is to make F stationary with respect to changes in $\phi(r)$ for $r<\sigma$.

An alternative derivation of the ORPA may be given using diagrammatic techniques.[11,33] This has the additional advantage of placing the ORPA and the closely related OCT into the context of other liquid state theories and to assess their exceptional usefulness.

Using the solution of Eq. (32) and combining it with Eq. (18) to describe the effect of the soft repulsions, we arrive at the following final result for the static-structure factor:

$$S(q)=S_\sigma(q)+\rho\hat{B}_\sigma(q)+\rho\,\delta\hat{h}(q) , \tag{34}$$

where the first term is the structure factor of the hard-sphere reference system, the second term corrects for the softness of the repulsion, and the third for the long-range attractive interactions.

The ORPA has been applied to a variety of potentials, such as the Lennard-Jones potential,[16–18] the square-well fluid[34,35] and to some selected liquid metals[36,37] and we refer to our recent paper on the square-well fluid[35] for the numerical details of the solution of the variational problem posed by Eq. (32).

The application of this technique to systems with *continuous* pair potentials poses a problem which does not arise for systems with pure hard-sphere repulsions and which has received only very little attention until now. The solution of Eq. (32) defines an optimized attractive potential $V_1'(r)$ given by [see Eqs. (8) and (30)]

$$V_1'(r)=\begin{cases}\phi(r), & r<0\\ V_{\min}, & \sigma<r<r_0\\ V(r), & r>r_0\end{cases} \tag{35}$$

and hence, in order to preserve the necessary condition

$$V(r)=V_0'(r)+V_1'(r) \tag{36}$$

we are forced to define a modified repulsive potential $V_0'(r)$ given by

$$V_0'(r)=\begin{cases}V(r)-\phi(r), & r<\sigma\\ V(r)-V_{\min}=V_0(r), & \sigma<r<r_0\\ 0, & r>r_0 .\end{cases} \tag{37}$$

This new repulsive potential $V_0'(r)$ must be used in the

WCA procedure to determine a new hard-sphere reference system V'_σ with a different hard-sphere diameter σ', which has then to be used in the ORPA procedure defining a new optimized attractive potential $V_1''(r)$—clearly this has to be repeated until a *self-consistent* separation of the total interatomic potential into a repulsive (short-range) part $V_0^{\mathrm{sc}}(r)$ and a long-range part $V_1^{\mathrm{sc}}(r)$ has been reached. The problem had been noticed by Andersen *et al.*,[18] but since in their calculations for the rather harshly repulsive Lennard-Jones potential they found that the first iteration changed σ only by a negligible amount [approximately $(1-2)\times 10^{-4}\sigma$], it was concluded that the iteration to self-consistency was not necessary. In our calculations with the rather soft alkali-metal pair potentials we find that the changes in σ are about 2 orders of magnitude larger [approximately $(1-2)\times 10^{-2}\sigma$] and we find changes in the ORPA contribution to the free energy of up to 4%. Hence the iteration of the WCA plus ORPA procedure to self-consistency is necessary. The convergence is quite rapid, after four iterations the hard-sphere radius and the free energy have converged to at least four leading digits.

IV. APPLICATION TO EXPANDED FLUID RUBIDIUM

In the following we shall discuss the application of the theory described in Sec. III to expanded fluid rubidium along the saturated-vapor-pressure curve. The calculations have been performed for a set of states for which experimental values of the static-structure factor are available. The temperature-volume relationship for the states investigated is given in Fig. 1.

The solution of the variational problem represented, in general, no difficulty, except at the lowest temperatures investigated. As the temperature approaches $T=350$ K we found that $n\beta\hat{V}_1(q)S_\sigma(q)<-1$ for q near Q_p (approximately the position of the first maximum of the static-structure factor). As a consequence the RPA-structure factor $S^{\mathrm{RPA}}(q)=S_\sigma(q)[1+n\beta\hat{V}_1(q)S_\sigma(q)]^{-1}$ diverges at these q values. At still lower temperatures, the RPA contribution to the free energy becomes negative and a solution of the variational problem turns out to be impossible: the functional $F(\delta h)$ diverges. This situation has been described by Wheeler and Chandler[39] under the name of "RPA catastrophe." They showed that in this situation (high density ρ, attractive interactions strong compared to the thermal energy, strong correlations in the reference system) the RPA free energy diverges in the thermodynamic limit. However, this thermodynamic instability is not the signature of a phase transition, but it is intimately related to the extremely unphysical description of the short-range correlations afforded by the RPA. At densities not too high, the ORPA corrects for the bad description of the short-range correlations, but at high densities the RPA is no longer a good starting point for the minimization of the free-energy functional $F(\delta h)$. No such problem arose at temperatures from $T=400$ K upwards, as long as $n\beta\hat{V}_1(q)S_\sigma(q)>-1$ for all q the minimization of $F(\delta h)$ using a gradient routine in a six-parameter space (see Ref. 35 for details) was straightforward.

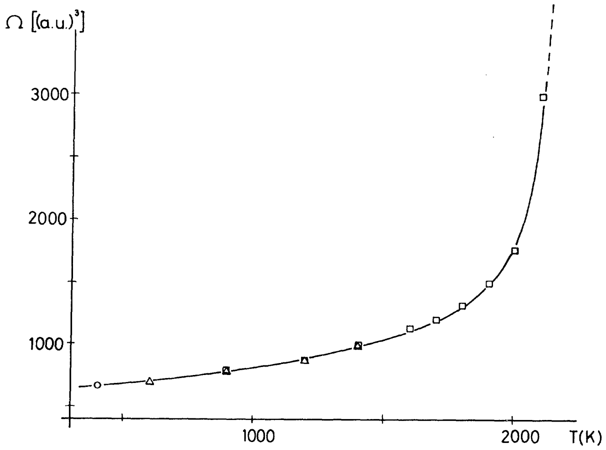

FIG. 1. Temperature vs atomic volume for the states investigated in this work. Squares, Franz *et al.* (Ref. 1); triangles, Mountain (Ref. 12); circles, interpolated density after Huijben *et al.* (Ref. 38). Dashed line, extrapolated.

The static-structure factors calculated at different levels of approximation are shown in Fig. 2 for a few representative states, the corresponding pair-correlation functions are given in Fig. 3. We see that the results vary very systematically with the degree of sophistication of the theory: Compared to the hard-sphere reference structure factor, the softness of the repulsive part of the pair potentials brings a weak damping of the first maximum and a relatively strong one of the higher-order oscillations, but no phase shift. At high densities, the main effect of the attractive forces is to order the fluid to a greater extent than in their absence. The higher degree of order shows up in the form of an enhancement of the height of the first maximum in $S(q)$. This effect is very strong in the RPA, it is weaker in the ORPA (this is an effect which is known as the "repulsive force screening" of the attractive interactions, Ref. 11), but still very important for a proper description of the experimental results. In addition, we observe a slight shift of the right-hand-side slope of the main peak and of the subsidiary oscillations to smaller values of q. Again this is just what is needed to get good agreement with experiment.

The effect of the attractive interaction on the short- and medium-range correlations in the fluid is seen much more clearly in the pair-correlation function (Fig. 3). As the function $B_\sigma(r)$ is localized in $\vec{r}$ space to the immediate vicinity of the hard-core diameter, the softness of the repulsive potential influences only the shape of the first peak in $g(r)$. The variation of the function with temperature and density is shown in Fig. 4. We find that the function becomes more extended with increasing temperature. As a consequence, the difference in the positions r_1 of the first peak in $g_\sigma(r)$ $(r_1=\sigma)$ and $g_{\mathrm{WCA}}(r)$ increases with increasing temperature. This effect just compensates for the decrease of σ with temperature (cf. below) so that the "nearest-neighbor distance" r_1 is essentially independent of the temperature, in agreement with experiment.[1,2] The

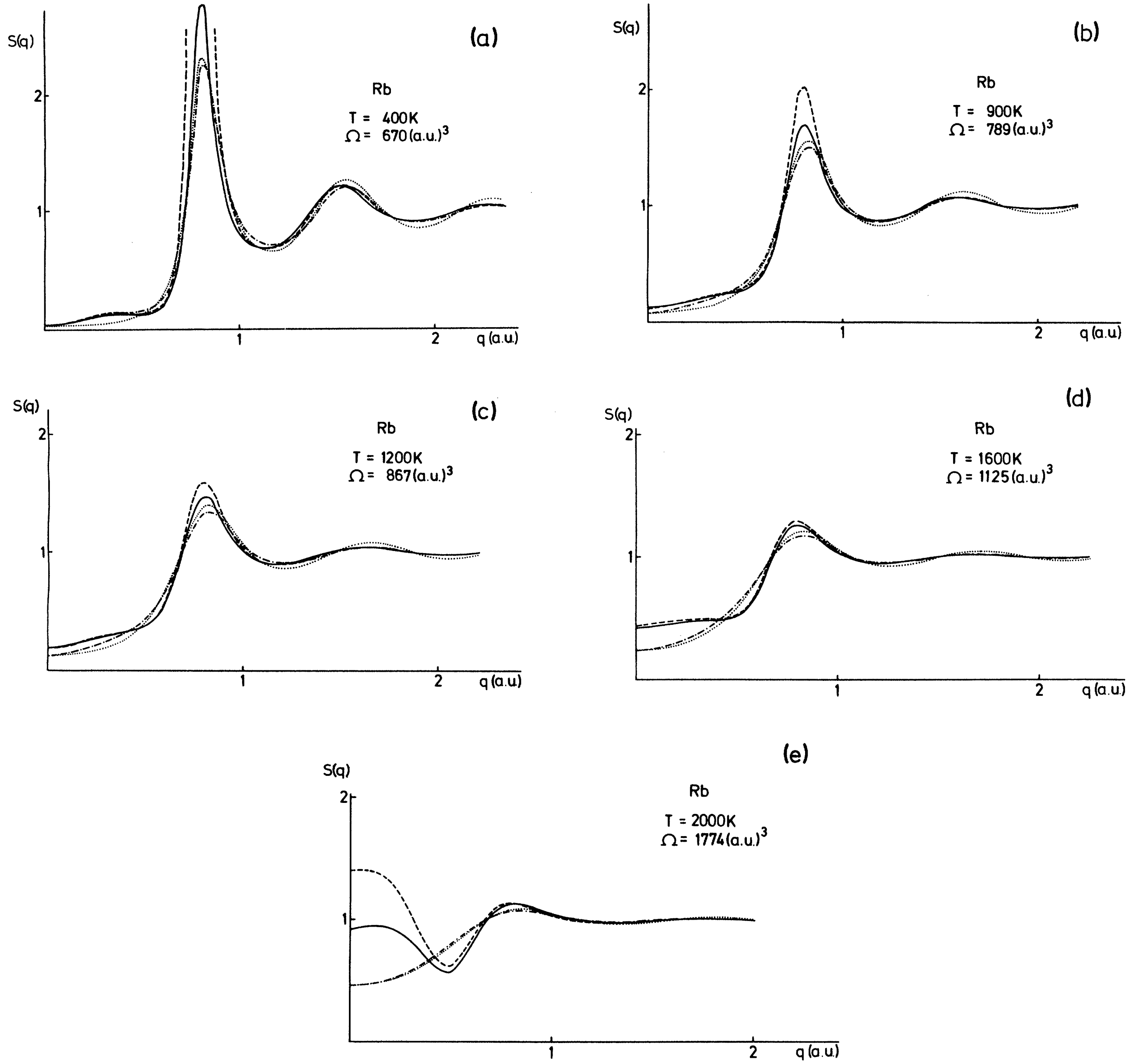

FIG. 2. Static-structure factor of expanded fluid rubidium for some states along the saturated-vapor-pressure curve. Dotted line, hard-sphere reference structure factor $S_\sigma(q)$; dotted-dashed line, $S^{\mathrm{WCA}}(q)=S_\sigma(q)+\rho\hat{B}_\sigma(q)$; dashed line, random-phase approximation $S^{\mathrm{RPA}}(q)=S_\sigma(q)+\rho\hat{B}_\sigma(q)+\rho\delta\hat{h}^{\mathrm{RPA}}(q)$; solid line, optimized random-phase approximation, $S^{\mathrm{ORPA}}(q)=S_\sigma(q)+\rho\hat{B}_\sigma(q)+\rho\delta\hat{h}^{\mathrm{ORPA}}(q)$.

variation of the effective hard-sphere diameter with temperature is dominated by the increase of the mean kinetic energy. We find that σ^{WCA} is always slightly larger than the mean collision distance σ^C determined by the relation

$$V(\sigma^C)=\langle E_{\mathrm{kin}}\rangle=\tfrac{3}{2}k_BT \tag{38}$$

which would be the result of a hard-sphere variational calculation.[8] The peak of the WCA pair-correlation function is situated at a distance which is just a bit smaller than r_0, due to the attractive interaction it is slightly shifted in the direction of the minimum. We find a very distinct influence of the oscillatory part of the pair potential on the short- and medium-range structure: wherever $V_1(r)<0$ we find $g^{\mathrm{ORPA}}(r)>g^{\mathrm{WCA}}(r)$, where $V_1(r)>0$ we find $g^{\mathrm{ORPA}}(r)<g^{\mathrm{WCA}}(r)$, which is just the physically plausible effect. Again this is overestimated by the RPA and reduced to realistic dimensions in the ORPA. Evidently the Friedel oscillations play a greater role in determining the liquid structure than the widespread use of the hard-sphere model suggests. In this respect we agree with the conclusions of Cummings and Stell[40] and Cummings and Egelstaff.[41]

The temperature variation of the long-wavelength limit of the static-structure factor is dominated by the attrac-

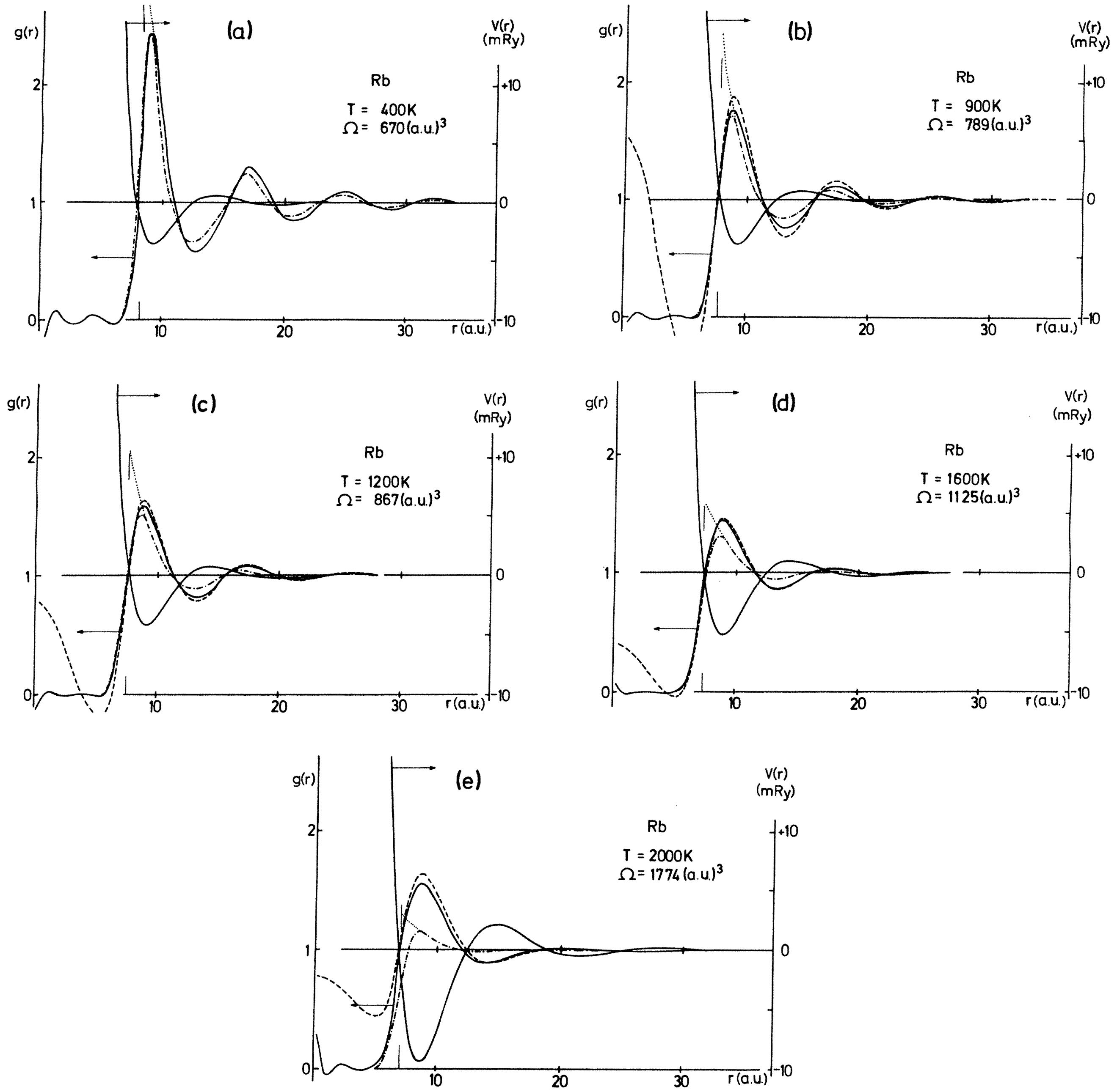

FIG. 3. Pair-correlation functions $g(r)$ corresponding to the static-structure factors shown in Fig. 2 (same symbols). Full interatomic pair potential is shown for comparison (right-hand-side scale).

tive interactions (Fig. 5). Already, at $T=900$ K, the contribution of $\delta\hat{h}(0)$ to $S(0)$ is about 50%. It is generally assumed that in the long-wavelength regime the RPA is a good approximation to the static-structure factor.[28,42,43] We find that this is justified only for temperatures sufficiently far from the critical region, at higher temperatures we have $S^{\mathrm{ORPA}}(0) \ll S^{\mathrm{RPA}}(0)$ (Fig. 2). Essentially the same conclusion has been reached by Henderson and Ashcroft.[44] They showed that the difference between the RPA and the exact $S(0)$ is related to the density derivatives of the reference structure factor. As the density dependence increases on approaching the critical region, we expect the RPA to become less reliable.

The critical point is characterized by a divergence of $S(0)$, i.e., of the compressibility. In our calculations we find that this divergence occurs at $T_c \simeq 2120 \pm 5$ K, whereas experimentally one finds $T_c = 2090 \pm 20$ K.[1,2] For a critical-point calculation, this is certainly quite good agreement. Very recently Gallerani *et al.*[45] and Cummings and Stell[46] have used the ORPA to study the critical behavior of Lennard-Jones and hard-sphere Yukawa fluids, respectively. Both studies point to a critical exponent $\gamma=2$ for the compressibility as in the three-dimensional spherical model, and in both studies it was

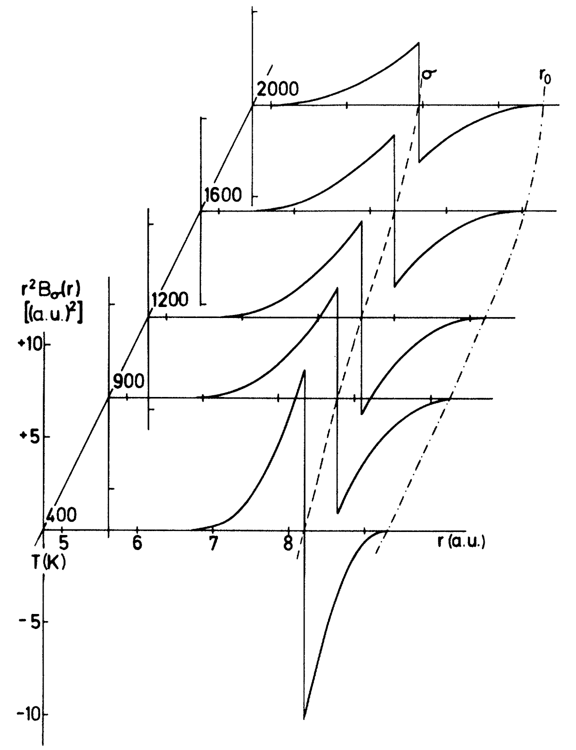

FIG. 4. Function $r^2B_\sigma(r)$ for liquid rubidium at different temperatures (see text).

found that the attractive part of the interatomic interaction introduces strong corrections to the leading term of the compressibility. A detailed investigation of the critical behavior is beyond the scope of the present paper, but the last finding may be relevant to our study: the strength of the interatomic potentials increases strongly with decreasing density. However, within the nearly-free-electron linear-response theory this increase is apparently still underestimated.

Finally, we compare our results with the neutron-scattering experiments of Franz *et al.*[1,2] (for $T=900$–2000 K) and of Waseda[47] (for $T=375$ K), see Fig. 6. For $T\leq 1400$ K we find a good agreement between theory and experiment for all momentum transfers, for $T\geq 1600$ K the agreement is still good for $q\geq 0.5$ a.u., but the long-wavelength density fluctuations are not adequately described.

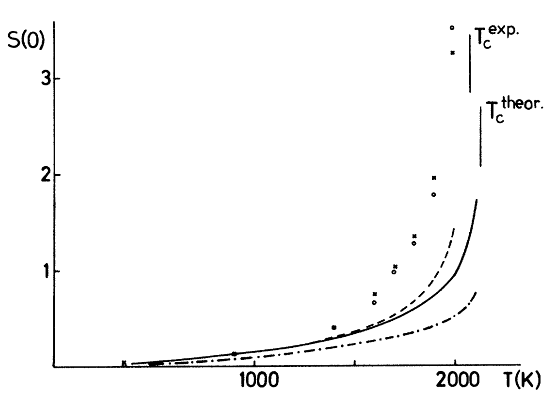

FIG. 5. Long-wavelength limit of the static-structure factor as a function of temperature: Solid line, ORPA; dashed line, RPA; dotted-dashed line, WCA-plus-hard-sphere calculation. Experiment: ○, $S(0)$ from p-V-T data; ×, $S(0)$ from diffraction data (Refs. 1 and 2).

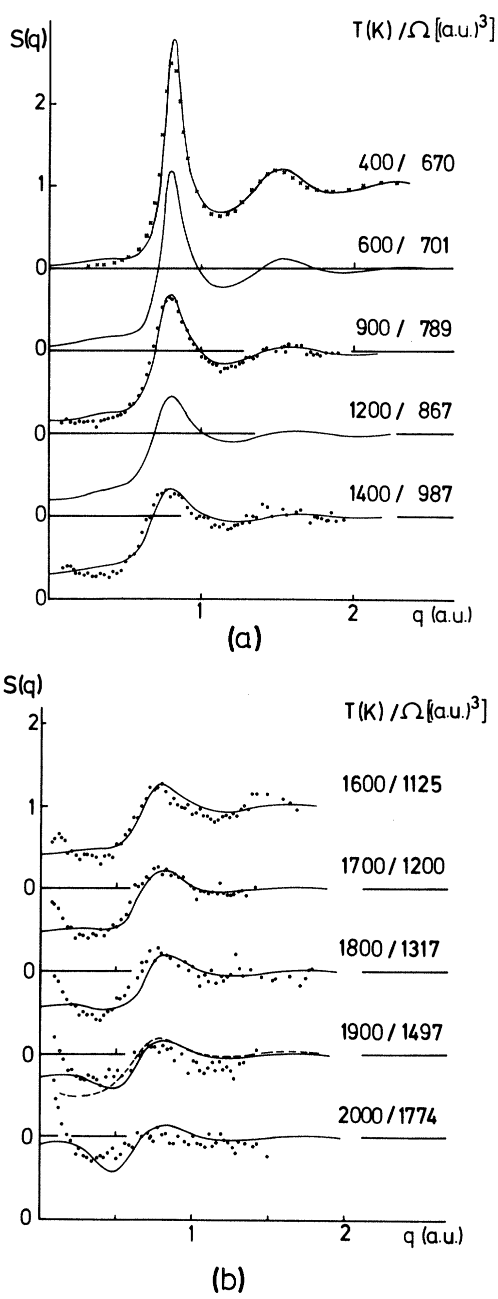

FIG. 6. Static-structure factor of expanded fluid rubidium at different temperatures. Solid lines, ORPA calculation. Open circles, neutron-scattering results of Franz *et al.* (Refs. 1 and 2); crosses, neutron-scattering results of Waseda (Ref. 47). For $T=1900$ K the result of the molecular-dynamics calculation of Tanaka (Ref. 13) is shown by the dashed line.

The good agreement we note for low and moderately elevated temperatures is important because it demonstrates that the WCA plus ORPA procedure is adequate even for pair potentials as soft as those of rubidium. Earlier conclusions that the WCA formalism is unable to cope with such extremely soft potentials[9,28] are shown to be premature: The disagreement between the WCA theory and experiment found in these papers is not to be attributed to a failure of the WCA scheme, but to the neglect of the attractive forces. Our results suggest that the oscillatory part of the interatomic potential plays an important role in determining the medium-range structure of liquid Rb; very recently we have obtained similar results for a number of liquid polyvalent metals.[48]

At higher temperatures, the attractive interactions are still very important in determining the form of the first diffraction peak. The fact that the nearest-neighbor distance r_1 and hence the peak position Q_p in $S(q)$ are independent of temperature (which arises from a compensation between a decreasing effective hard-core diameter and an increasing softness of the potential) is confirmed by the experiment. The form of the long-wavelength part of $S(q)$, however, is not in agreement with experiment. In this respect it is interesting to make a comparison with the computer simulations of Tanaka[13] and Mountain.[12] Although, due to the limited size of the samples, the extreme low-q limit is not accessible to the simulations, we see that again the long-wavelength density fluctuations are not adequately reproduced, although the large-q part of $S(q)$ is quite accurate. This allows us to conclude that the failure to reproduce the temperature dependence of $S(0)$ is not to be blamed on the ORPA alone. Hence we find two reasons.

(i) The density dependence of the interatomic potentials is evidently underestimated for $T \geq 1400$ K. This has nothing to do with the local field factor $G(q)$ in the dielectric function. Our potentials calculated using the Ichimaru-Utsumi $G(q)$ (Ref. 25) are more attractive than the interatomic potentials constructed by Tanaka[13] and by Mountain[12] using the $G(q)$ of Singwi *et al.*, but this has only little influence on the structure factor. Note that at this temperature and at saturation density the electrical resistivity reaches a value of $\rho \sim 300$ $\mu\Omega$ cm—hence the mean free path of the electrons is of the order of magnitude of the interatomic separation and the linear screening approximation breaks down. At about the same temperature and density the temperature coefficient of the electrical resistivity becomes negative,[2] marking the onset of the metal-insulator transition. This also correlates with the observed paramagnetic susceptibility.[19] A simple calculation of the electrical resistivity along the saturation curve using the Faber-Ziman theory and our pseudopotentials and static-structure factors yields a good agreement with the experimental results again up to $T \sim 1400$ K (Fig. 7). For higher temperatures the calculated resistivities lie substantially above the experimental values. This is typical for the breakdown of the weak-scattering Faber-Ziman theory in a strong-scattering situation. An improved transport theory for these high-resistivity conductors has recently been developed by Belitz and Schirmacher.[49] They show that with increasing static and thermal disorder the electron propagators entering the resistivity formula begin to deviate from those for free electrons. As the same electron propagators also enter in the linear-response calculation of the interatomic potentials, we conclude that at these high temperatures the screening function must be corrected for the short electronic mean free path.

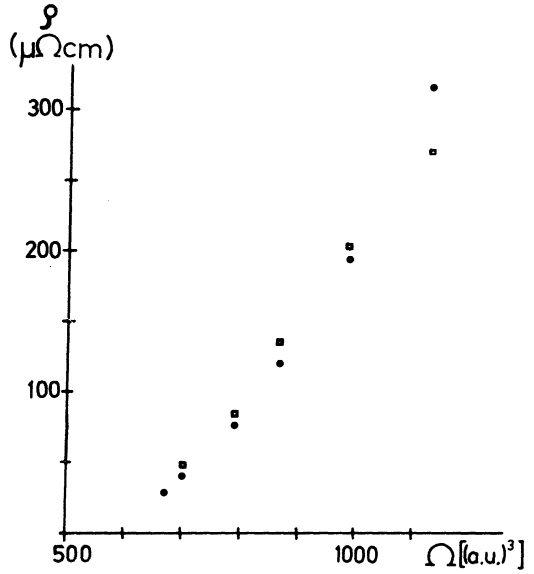

FIG. 7. Variation of the electrical resistivity along the saturation curve: circles, ORPA results; squares, data taken from Franz (Ref. 2).

(ii) Our calculation refers to the experimental saturation curve—which is not necessarily identical with that of the system described by our set of pair potentials. Thus there is at least the possibility that our $\Omega(T)$ curve bypasses the critical point and hence shows weaker density fluctuations. Finally, there is still the possibility of exploring more complete diagrammatic expansions such as the optimized cluster theory.[11] However, the algorithms required to obtain the solution of the OCT for continuous potentials[33] will be necessarily more complex than those presently employed for the solution of the ORPA.

V. CONCLUSIONS

We have the following.

(i) At low and moderately elevated temperatures the ORPA gives a good description of the structure.

(ii) The effect of the oscillatory potential is to order the liquid by forcing the atoms into the attractive wells of the potential.

(iii) The critical temperature is calculated relatively accurately [$T_c = 2120 \pm 5$ K (theor.) against $T_c = 2090 \pm 20$ K (expt.)], but the onset of the long-wavelength density fluctuations is confined to a narrower temperature interval than observed experimentally.

(iv) The nearly-free-electron approximation breaks down at the density where the mean free path becomes of the order of magnitude of the interatomic distance—below this density the true potential is much more attractive than the one given by the linear-response calculation.

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