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Analysis of the structure of molten germanium from local and nonlocal pseudopotentials

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We show that the nonlocal pseudopotential theory with no adjustable parameter fairly well predicts the complex structure of liquid germanium. This establishes more firmly the validity of the local pseudopotential approach, which implies a fine adjustment of the parameter of the model.

The structure of liquid germanium shows several peculiar tendencies which are well differentiated by the x-ray and neutron experiments.[1-3] These peculiarities are (i) the low coordination number $N_c \simeq 6.5$ ($N_C \simeq 11$ for most liquid metals), (ii) the intermediate maximum situated between the first two peaks of the pair correlation function $g(R)$, and (iii) the broad shoulder on the high-wave-number side of the first peak of the structure factor $S(q)$.

These features have been interpreted by Kahl and Hafner[4,5] on the basis of the local pseudopotential theory by using the empty-core model (ECM) to describe the ion-electron interaction[6] and the optimized random-phase approximation (ORPA) to calculate the liquid structure.[7] These authors explain the shoulder in $S(q)$ by the competition of two length scales, i.e., the hard-core diameter stemmed from the repulsive part of the pair potential $V(R)$ and the Friedel wavelength which characterizes the oscillatory part of $V(R)$. Another study has been carried out by Aers *et al.*[8] with the aid of the modified hypernetted-chain integral equation (MHNC) to calculate the structure factor, but they adjust both the radius R_c of the ECM and the electron density parameter r_s until they obtain a better fit of $S(q)$. They argue that a fine interplay between $S(0)$ and r_s is essential to the generation of the shoulder in $S(q)$.

In summary, an accurate adjustment of one or several parameters seems necessary to reproduce the experimental structure factor including the shoulder on the first peak. However, this reveals a weakness of the local pseudopotential theory which can be eliminated with a nonlocal pseudopotential containing no adjustable parameter. Consequently, the connection between the feature of the ionic core and the structure will be more firmly established from such a theory. In this Brief Report we present our results for Ge when considering the nonlocal optimized model potential[9] (OMP) and the ORPA, following the technique developed in Ref. 10. We analyze the respective contributions of the repulsive and oscillatory parts of $V(R)$ on $S(q)$ and $g(R)$ and we also briefly discuss the possibility of producing similar results with the ECM.

In order to calculate the pair potential from the pseudopotential theory we only consider the expressions, in atomic units, which are relevant to our discussion,

$$V(R)=\frac{(Z^*)^2}{R}\left[1-\frac{2}{\pi}\int_0^\infty F_N(q)\frac{\sin(qR)}{q}dq\right], \quad (1)$$

where Z^* is the effective valence and F_N (q) is the normalized energy–wave-number characteristic. For the OMP, F_N (q) cannot be reduced to a simple product of various factors and all the basic ingredients necessary to the computation of this quantity are developed in Ref. 10. The parameters of the OMP, which are fully calculated from the known ionic energy levels and Fermi level in the liquid state, are given in Table I.

In the local theory, the normalized energy-wave-number characteristic is defined by

$$F_N(q)=\left[\frac{\Omega q^2}{4\pi Z}\right]^2 w^2(q)\frac{1}{1-G(q)}\left[1-\frac{1}{\epsilon(q)}\right], \quad (2)$$

where Z is the actual valence, Ω is the atomic volume, and $\epsilon(q)$ is the dielectric function including the exchange-correlation factor $[1-G(q)]$. For this purpose, we only adopt the Ichimaru and Utsumi[11] expression of $G(q)$ as well as the ECM

TABLE I. Parameters of the OMP for liquid Ge at its melting temperature ($T_M = 1210$ K, atomic volume $\Omega = 148.24$ a.u., well depth A_l, derivatives with respect to energy $\partial A_l/\partial E$, effective masses m_e, m_k, effective valence Z^* and radius of the uniform depletion hole R_d).

A_0	A_1	A_2	$-\frac{\partial A_0}{\partial E}$	$-\frac{\partial A_1}{\partial E}$	$-\frac{\partial A_2}{\partial E}$	m_e	m_k	Z^*	R_d
2.169	2.486	2.069	0.406	0.161	0.404	0.9484	0.7383	4.223	1.815

$$w(q)=-\frac{4\pi Z}{\Omega q^2}\cos(qR_{c,})\ . \qquad (3)$$

In principle, the parameter R_c would be the ionic radius ($\simeq 1$ a.u. for Ge), but in practice it is adjusted to fit a peculiar macroscopic property. Here we have considered three values of R_c. (i) $R_c=1.03$ a.u., which is used in Ref. 5, corresponds to the model labeled ECM1. (ii) $R_c=0.977$ a.u. is obtained when adjusting the first node of the ECM form factor on that of the OMP form factor. It is labeled ECM2. (iii) $R_c=0.846$ a.u., labeled ECM3, satisfies the condition $4K_FR_c=\pi$, where K_F is the Fermi wave vector in the liquid state, so that the Friedel oscillations at large R are fully damped since

$$V_{\mathrm{ECM}}(R\to\infty)\simeq[\cos(2K_FR_c)]^2\cos(2K_FR)/R^3\ . \qquad (4)$$

Of course, such a value of R_c is not realistic for normal Ge, however, it can serve to analyze the amplitude effect of the Friedel oscillations on the structure.

In Fig. 1 we compare the effective pair potentials issued from the local and nonlocal pseudopotentials. Although the OMP results cannot be completely reproduced by the unique adjustment of R_C in the ECM, they can be fitted as close as possible. Thus a good agreement is obtained between ECM2 and OMP curves, while if R_c increases (ECM1) the oscillations in $V(R)$ are substantially larger than in OMP. On the contrary, a reduction of R_c induces oscillations progressively damped and shifted towards the origin with a marked displacement of the position of the first minimum. It is also worth noting the point of inflexion in the repulsive part of $V(R)$, which is very apparent in the OMP but vanishes in the ECM2.

To calculate the structure factor, the ORPA method requires the knowledge of the hard-sphere diameter of the reference system, which is determined self-consistently from the blip function expansion (WCA approximation[12]). To perform this calculation, one usually adopts the separation of the pair potential at the position of the first minimum (R_m). Nevertheless, in liquid Ge, the main peak of $g(R)$ lies at the position $R_i\simeq 5.3$ a.u., which is much smaller than R_m. Thus a good convergence of the blip function expansion implies the choice of a separation of the potential close by R_i. However, since the ORPA procedure is a double perturbation scheme, there is some flexibility in the choice of R_i.[4,10] In the present work we choose R_i at the inflection point of $V_{\mathrm{OMP}}(R)$, i.e., 5.5 a.u., and we keep the same value for the other pair potentials. Therefore the perturbation of

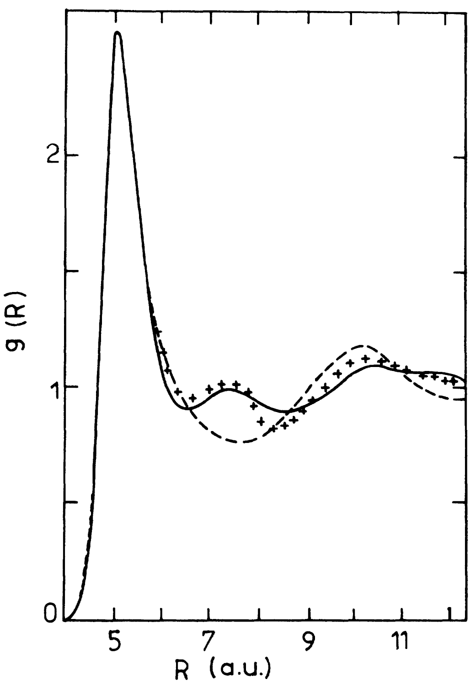

FIG. 2. Modifications of the pair correlation function due to the tail of $V_{\mathrm{OMP}}(R)$: dashed line (WCA, $R<5.5$ a.u.), crosses (ORPA, $R<7.35$ a.u.), solid line (ORPA, $R<10.55$ a.u.).

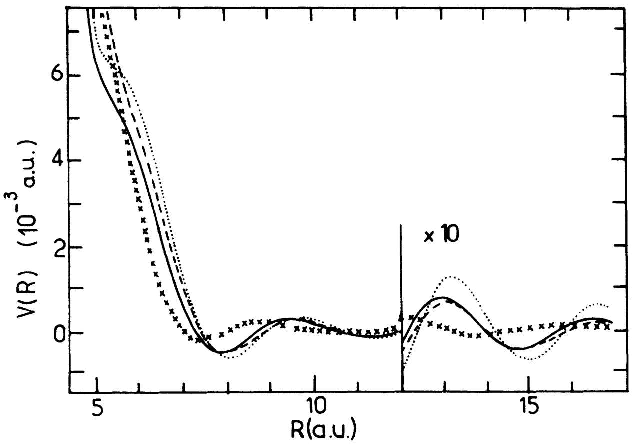

FIG. 1. Pair potential of normal liquid Ge at its melting temperature: Solid line (OMP), dotted line (ECM1, $R_c=1.03$ a.u.), dashed line (ECM2, $R_c=0.977$ a.u.), crosses (ECM3, $R_c=0.846$ a.u.).

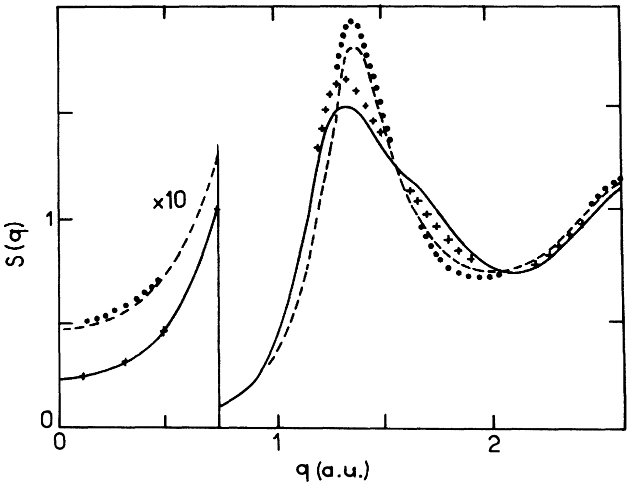

FIG. 3. Modifications of the structure factor due to the tail of $V_{\mathrm{OMP}}(R)$: dots (HS reference system), dashed line (WCA, $R<5.5$ a.u.), crosses (ORPA, $R<7.35$ a.u.), solid line (ORPA, $R<10.55$ a.u.).

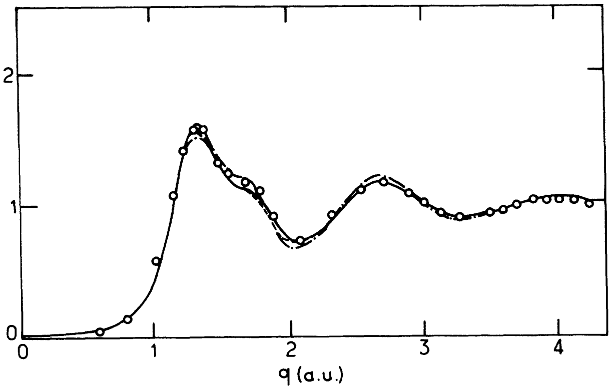

FIG. 4. Structure factor of normal liquid Ge at its melting temperature: Solid line (OMP), dash-dotted line (ECM1), dashed line (ECM2), open circles [experiment, Waseda (Ref. 2)].

$V(R)$ contains a short-range repulsive ledge. Indeed, the hard-sphere diameters are practically the same for all the potentials of Fig. 1, namely $\sigma_{\text{OMP}} = 4.78$ a.u., $\sigma_{\text{ECM1}} = 4.83$ a.u., $\sigma_{\text{ECM2}} = 4.80$ a.u., and $\sigma_{\text{ECM3}} = 4.78$ a.u.

To know which part of $V(R)$ is the most influential for the salient details of the liquid germanium structure, we truncate the tail of $V(R)$ at the successive nodes 7.35, 8.85, 10.55 and 15.9 a.u. Consider first the pair correlation function $g(R)$, in Fig. 2. It is clear that an intermediate maximum, between the first two peaks, occurs as soon as the repulsive part of $V(R)$, within the range $R_i < \text{R} < 7.35$ a.u., is taken into account whereas all the further oscillations in $V(R)$ do not strongly modify the behavior of $g(R)$. On the contrary, the presence of the shoulder in $S(q)$ (Fig. 3) depends on the Friedel oscillations, since the progressive construction of such a hump is the signature of the long-range component parts of $V(R)$. Besides, it may be seen that the low-q region of $S(q)$ is essentially determined by the ledge of the $V(R)$ tail. Thus the reduction of S(0), from the WCA value (0.048) to 0.027, as well as the displacement of the main peak of $S(q)$ from the WCA position, can be attributed to the $V(R)$ part located in the range $R_i < \text{R} < 7.35$ a.u. and not to the oscillations.

Let us briefly examine the influence of the local pseudopotential parameter R_c on the structure factor. Figure 4 shows that the structure factors issued to the OMP and ECM2 are very close to each other, even at q=0, since S(0) is equal to 0.027 for OMP and 0.024 for ECM2. In the case of ECM3 (not displayed in Fig. 4), there is neither shoulder nor asymmetry in the main peak; this shows the importance of the adjustment of the parameter R_c, when a local pseudopotential is used.

TABLE II. Coordination number (N_c) and resistivity (ρ) of liquid Ge.

	N_c	ρ ($\mu\Omega$ cm)
OMP	7.1	52
ECM2	7.1	54
$R_c = 0.977$ a.u.		
ECM1	7.2	47
$R_c = 1.03$ a.u.		
Expt.	6.5,[a] 7[b]	68[c]

[a] Reference 1.
[b] Reference 2.
[c] Reference 14.

Now comes the question of the best agreement with the experiment. Figure 4 and the corresponding $g(R)$, not shown, suggest that the ECM2 and the OMP are equally good and both better than the ECM1. However, we must be careful in any definite conclusion since there are some systematic differences between the x-ray diffraction and neutrons diffusion results for liquid metals due to the discrepancies in the scattering mechanism.[13] In particular Bellissent-Funel and Bellissent[3] observed a smaller intensity for the main peak of $S(q)$ in their neutrons scattering experiment. An interesting complementary test for the distribution functions is the calculation of properties which imply the integrals of $g(R)$ and $S(q)$ such as the coordination number N_c and the Faber-Ziman expression of the resistivity ρ. The values which are listed in Table II confirm that the OMP and ECM2 are slightly better predictors than the ECM1.

In conclusion, we have shown that, if the HS diameter is correctly chosen to generate the crudest shape of $g(R)$ and $S(q)$, the peculiar features of $g(R)$ and $S(q)$ can be reproduced by the oscillatory part of $V(R)$, without invoking special parameters. Nevertheless, the fair description of the liquid structure factor, which is obtained from local ECM, can be explained because the single adjustment of the parameter R_c allows a close matching of the Friedel oscillations to the pair potential stemmed from the nonlocal OMP. This very particular success of local theory, for Ge, would be interesting for the study of Ge alloys, provided that the other elements are equally well described by the local theory.

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