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Test of transferability of the evanescent core pseudopotential from solid state to liquid state

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We present the results of a test of transferability of three versions of the local evanescent core (EC) pseudopotential constructed by Nogueira, Fiolhais, and Perdew [Phys. Rev. B **59**, 2570 (1999)] for the solid state. The test is a quantitative analysis of the static structure factor and the velocity autocorrelation function of rubidium along the liquid-vapor coexistence curve predicted by molecular dynamics simulation. The results clearly show that the individual EC pseudopotential predicts the structure of the bulk liquid metal in good agreement with the experimental data, while the two universal EC pseudopotentials give an unsatisfactory description of the liquid state due to the drastic change of the effective pair potential that occurs with decreasing density.

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The static and dynamic properties of liquid metals can be successfully investigated by standard simulation techniques provided that effective interionic potentials are available. Clearly, these potentials are density dependent and exhibit long-range Friedel oscillations that are a manifestation of the Fermi surface of the conduction electrons. Both features have to be dealt with careful treatment. Especially for simple metals, interionic potentials are well justified for most properties and their functional form is well established from the pseudopotential concept. In the last twenty years, the significant success of liquid-state theory in examining the detailed properties of liquid metals is due to the pseudopotential approach[1–3] to a large extent.

For most theoretical models of simple metals, the electron-ion interaction is replaced by a weak scattering pseudopotential, which is often chosen to take the form of square well inside a certain radius and take the Coulomb interaction expression outside this radius. Two main routes are used to construct pseudopotentials : (i) in computing the pseudopotential directly from information about atomic spectra or atomic calculations and (ii) in forcing the pseudopotential to reproduce some measured properties of the system. It is intriguing that pseudopotentials derived from a specific property can be used to determine either another property or the same property of the system in a different chemical environment. Thus, one must be cautious in transferring pseudopotentials from the solid state to the liquid state, in spite of successful calculations.

Recently, Fiolhais *et al.*[4] proposed a local pseudopotential fitting three dominant density parameters for 16 simple metals in the solid state: (i) the valence Z, (ii) the radius r_s of the sphere, which on average contains one valence electron, and (iii) the electron number N_{int} averaged over the interstitial region between the Wigner-Seitz polyhedron and the largest inscribed sphere. In contrast to many other models, this local pseudopotential is constructed so that (i) the core repulsion presents a exponential decay at large distances and (ii) the suitable core potential smoothly joins to the resulting potential outside the core. For each element, the pseudopotential is fixed by two parameters R and α, which are chosen by using either the conventional crystal structure (individual parameters) or the fcc structure (universal parameters). With the imposed conditions, the pseudopotential contains no adjustable parameters. The so-called evanescent core (EC) pseudopotentials of Fiolhais *et al.*,[4] namely, EC(I) and EC(U1), have the definite advantages of predicting correctly binding energies, bulk moduli and their pressure derivatives, chemical potentials and phonon frequencies in solid state,[5,6] as well as the resistivity[7] and the ionic structure[8,9] in liquid metals, and the melting of a quasi-2D metallic system[10] though the pseudopotential is optimized for the bulk solid state environment. Recognizing later that the parameters R and α depend on the valence Z and the average electron density ρ $[=3/(4\pi r_s^3 Z)]$, Nogueira, Fiolhais, and Perdew[11] propounded a new version of the universal evanescent core pseudopotential [EC(U2)] in which the parameters $R(r_s,Z)$ and $\alpha(r_s,Z)$ are tabulated functions of r_s and Z. Recently, Chekmarev, Oxtoby, and Rice[12] have questioned the adequacy of the EC(U2) model to predict the structure of inhomogeneous liquid metals. Their conclusion is that it is necessary to carry out the simulations at unphysical temperatures to achieve a good agreement with the measured pair correlation functions.

In this paper, our intent is to examine the extent to which the three versions of the evanescent core local pseudopotential EC(I), EC(U1), and EC(U2), can be transferred successfully from the solid state to the liquid state. In the pseudopotential formalism, the density dependence of the effective pair potential in simple liquid metals enters through the screening effects of the valence electrons and, occasionally, through the pseudopotential parameters $R(r_s,Z)$ and $\alpha(r_s,Z)$. A direct probe of the transferability of the EC pseudopotential is possible in considering the ionic positional correlations obtained from the static structure factor. Among alkali metals, rubidium is the most extensively studied fluid in the literature and its structure factor has been measured for a wide range of temperatures and densities.[13–15] Here we have calculated the structure factor $S(q)$ and the velocity autocorrelation function (VACF) $\psi(t)$ of rubidium by molecular dynamics (MD) simulation for some thermodynamic states along the liquid-vapor coexistence curve where the density changes drastically. This choice

TABLE I. Thermodynamic states investigated in this study: temperature *T*, density *d*, and radius of the electronic sphere r_s (a.u.: atomic units).

State	I	II	III
T (K)	373	773	1373
d (g cm^{-3})	1.45	1.28	0.99
r_s (a.u.)	5.404	5.740	6.179

is crucial to test the transferability of the EC pseudopotential from one physical property to another and from one environment to another. The required elements of the pseudopotential theory are discussed at length in Refs. 1–3 and will not be repeated here. For useful details about the construction of an effective pair potential and the MD calculations of the structure factor and the VACF, the reader is referred to our previous articles.[9,16]

For the purpose of discussion, we show in Table I the relevant input data concerning three thermodynamic states of expanded fluid Rb. The states considered (373, 773, and 1373 K) are selected among those investigated recently by Hosokawa *et al.*[15] from the triple point up to a limit far below the critical point, where the metallic behavior of Rb is certain. It is commonly accepted that the Friedel oscillations persist into the effective pair potential at mass densities of about 2–3 times the critical density ($d_c = 0.29$ g cm^{-3}). Note that the parameters of the EC(U2) pseudopotential are extracted from an AIP document[17] in which R and α are tabulated for several values of the radius r_s and the valence Z. One further important aspect of the pseudopotential approach for evaluating the effective pair potential is the choice of the local-field correction accounting for the density dependent exchange-correlation effects.[18] In all our calculations, we have used the local-field correction of Farid *et al.*[19] established by fitting the equation of state of the uniform electron gas.

Figure 1 shows the density dependence of the effective pair potentials issued from the three specified versions of the pseudopotential. Actually, in spite of the fact that both the temperature and the mass density vary simultaneously along the liquid-vapor coexistence curve, the relevant parameter for the variation of the pair potential $u(r)$ is the electron density related to r_s. Here we attempt to determine to what extent the success of the effective pair potential could be attributed to the density dependence of the parameters of the pseudopotential. Considering at first the EC(I) and EC(U1) models, we observe an enhancement of the first potential well and a shift of the first zero towards small distances, as the electron density decreases. It is interesting to note that the second zero of $u(r)$ for the EC(I) model is fixed contrarily to what happens for the EC(U1) model. Also, it is found that the potential well is somewhat deeper for the EC(I) model than for the EC(U1) one whereas its repulsive part is harder. Turning to the long-range oscillatory tail, these two potentials look similar because the density dependence of the Friedel oscillations is evident through the asymptotic form of $u(r)\{\sim[w(2k_F)]^2\cos(2k_F r)/r^3\}$, where the Fermi wave vector $k_F \sim \rho^3$. The amplitude but not the phase depends on the form factor of the pseudopotential $w(2k_F)$ evaluated on the Fermi surface.

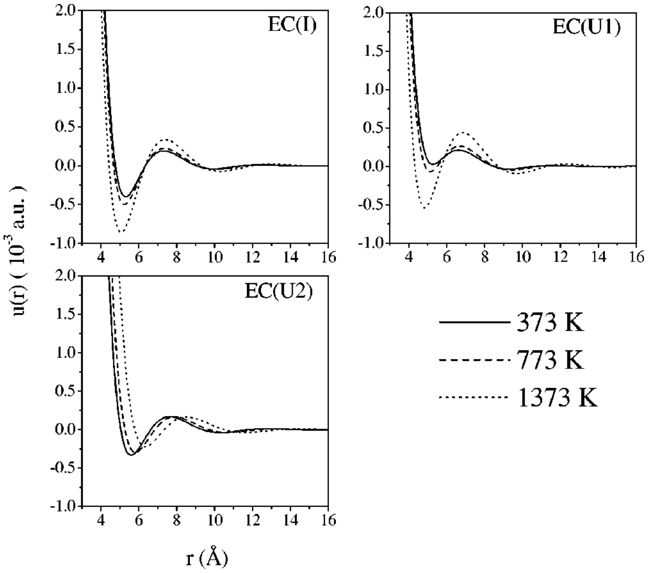

FIG. 1. Interionic pair potentials for the three thermodynamic states investigated with each kind of parameters studied.

We now examine the interionic potential coming from the EC(U2) model. The major difference with respect to the EC(I) and EC(U1) models, which is revealed by inspection of Fig. 1, is a shift of the interionic potential towards large distances as the electron density decreases. For a quantitative analysis of the shifting, we have shown, in Table II, the position σ of the first zero of $u(r)$ and the well depth ε of its first minimum for the three potentials under study. Among interionic potentials widely used for liquid metals, the one of Price, Singwi, and Tosi[20] based on the local pseudopotential of Ashcroft[21] has been used extensively with success in studying the static and dynamic properties of liquid alkali metals.[22–24] Other nonlocal pseudopotentials have also been found to be quite successful for describing the structural properties of expanded Rb.[25–27] A comparative analysis of the discernible features of the interionic potentials points out that the effective potential issued from the EC(U2) model does not have the necessary density dependence because of its important shift towards large distances as the electron density decreases, contrarily to that of the other potentials. We consider *a priori* this change to be anomalous although an increase of the nearest-neighbor distance is expected intuitively since, in liquid metals, the geometrical arrangement of the ions generally does not change with density and the interionic distances vary as $\rho^{-1/3}$.

To test the adequacy of the EC pseudopotential, it is now desirable to use the three resulting interionic potentials to calculate some properties of liquid Rb such as the structure factor and the VACF using the molecular dynamics simulation. Following our previous work,[9] we have adopted the Verlet algorithm in the velocity form and the standard periodic boundary conditions. Particles are initially located on a fcc lattice, and the cutoff radius is chosen between 2.5 and 3 times the first zero distance of $u(r)$. According to Allen and Tildesley,[28] long-range corrections such as Ewald summation

TABLE II. Pseudopotential parameters α and R (a.u.: atomic units). Interionic potential features: position of the first node σ, depth of first well ε, and Grüneisen parameter γ_G. Coordination number N and self-diffusion coefficient D.

EC type	State	α	R (a.u.)	σ/r_s	ε	N	D (10^{-8} m^2 s^{-1})	γ_G
I	I	3.197	0.760	0.883	-3.988	7.01	0.35	2.09
	II	3.197	0.760	0.822	-4.991	5.80	1.78	1.98
	III	3.197	0.760	0.722	-8.593	3.77	6.03	1.75
U1	I	2.749	0.823	/	$+0.259$	6.61	0.57	2.68
	II	2.749	0.823	0.848	-0.716	5.02	2.39	2.35
	III	2.749	0.823	0.702	-5.410	3.09	6.49	1.82
U2	I	3.205	0.800	0.942	-3.320	7.02	0.10	2.16
	II	3.152	0.848	0.922	-2.952	5.68	1.71	2.18
	III	3.082	0.933	0.945	-2.226	5.83	3.96	2.22

method are useless when $u(r)\sim r^{-3}$ for large r. Two systems have been used, respectively, with 256 particles for the simulation of the dynamic properties and 2048 particles for the static properties in order to obtain a large enough extension of the pair correlation function $g(r)$. In both cases, the length of the simulation is chosen such that the uncertainty on $g(r)$ and $\psi(t)$ is less than 1% while the Fourier transform might increase it a few percent in the low-q range of $S(q)$.

The most interesting features of the observed density dependence of expanded Rb structure are a linear decrease of the coordination number and a virtually unchanged position of the first peak of $g(r)$ when the density is decreased along the liquid-vapor coexistence curve. The agreement between theoretical and experimental results for $g(r)$—not shown here—is reasonably good, especially for the EC(I) model, taking account of the inaccuracy due to numerical Fourier transform of the experimental data. To investigate in more details the blurring of the liquid structure during the expansion, we performed the calculation of the coordination number N. As can be seen from Table II, N decreases linearly with decreasing density for the EC(I) model in accordance with the experimental findings, whereas it remains quite unchanged between 1.28 and 0.99 g cm^{-3} for the EC(U2) model.

To carry out a more precise comparison between theoretical results and experiments, another crucial structural characteristic of expanded Rb is the density dependence of the structure factor. Once the simulated pair correlation functions $g(r)$ are obtained, we proceed next to calculate the structure factors $S(q)$ by performing Fourier transform of $g(r)$. Comparisons of the theoretical results of $S(q)$ with the recent x-ray diffraction measurements,[15] starting from wave numbers greater than 0.5 Å^{-1}, are shown in Fig. 2 for the three thermodynamic states investigated. Just above the melting point, it should be noted that the position of the first peak of $S(q)$ is quite well predicted by the three EC models while its magnitude is correctly reproduced by the EC(I) model only. In contrast, the greatest discrepancy is observed for the EC(U2) model for which the amplitude of the first peak is overestimated. It is clearly evident that the best agreement is obtained with the EC(I) model even if it slightly deteriorates for the lowest density. Such a discrepancy is not surprising as it is well known that a pseudopotential cannot describe an expanded metal near the critical point. The reason is that the metal-nonmetal transition, which occurs along the liquid-vapor coexistence curve, is caused by

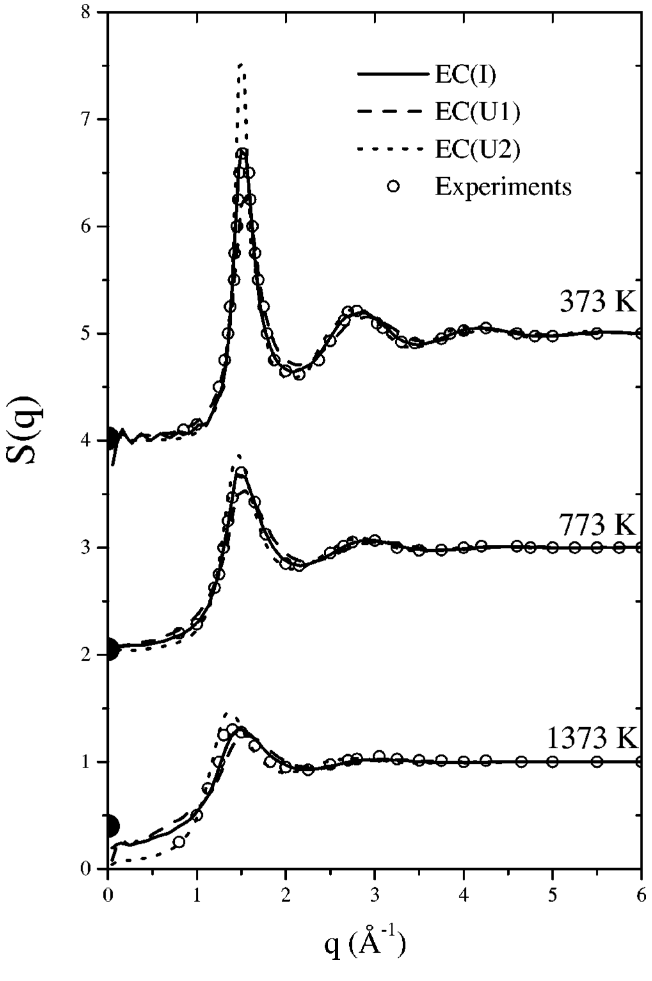

FIG. 2. Structure factor for each state with each set of parameters and compared with experiments. The curves are vertically shifted by an amount of 2. Experimental uncertainty is not published by Hosokawa *et al.* (Ref. 15). Full dots correspond to the experimental low-q limit reported by Matsuda *et al.* (Ref. 29).

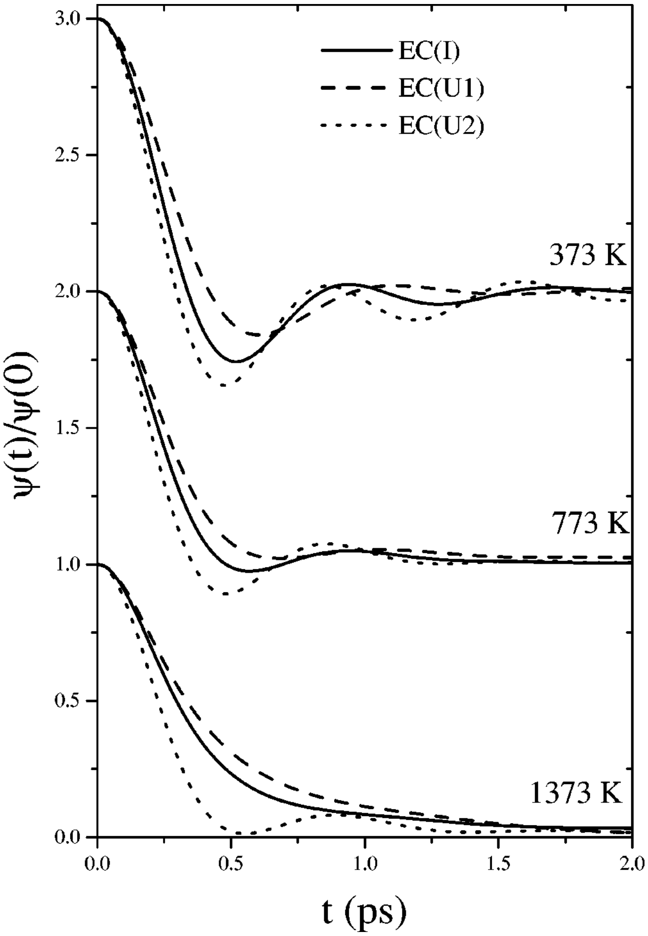

FIG. 3. Normalized velocity autocorrelation functions. Each set of curves are vertically shifted by an amout of 1.

a drastic change of the electronic structure leading to a modification of the long-range interionic potential. In addition, it cannot be ruled out that the low-q behavior of $S(q)$, especially as the density fluctuations intensify, is subject to the inherent difficulties of the MD simulation such as the limited number of particles. As compared to other theoretical works for expanded Rb, our results of $S(q)$ stemmed from the EC(I) model are better than those of Matsuda *et al.*[29] obtained from their local pseudopotential, and as good as those of Cheng, Chen, and Lai[26] obtained from a nonlocal pseudopotential using MD simulation.

We now continue to probe the importance of the density dependence of the EC pseudopotential in examining the evolution of the VACF of Rb as a function of the electron density. As for the structure factor, no model is invoked to calculate $\psi(t)$. With MD simulation, we have optimum conditions to provide accurate information on this particular individual dynamic property and to focus on the important issue of the density dependence of the interionic potential. Figure 3 displaying the results of such simulations for the three EC models indicates a drastic change in the form of the VACF as the electron density decreases. The common features of $\psi(t)$ in simple liquid metals near the melting point are a negative minimum followed by an oscillatory decay that reflects the nature of the actions by surrounding neighbors. This negative correlation region found to be present only in very dense fluids can be pictorially interpreted as being due to the bounce of the tagged particle against the cage formed by its nearest neighbors. This feature appears to be consonant with the solid-state picture used to understand the mechanisms of single-particle dynamics in liquids. However, the oscillatory feature of $\psi(t)$ reduces as the electron density decreases, approaching a slow decay predicted by the theory to be directly proportional to $t^{-3/2}$ at rather long times. Thus, at low electron densities, the particles in front of the tagged particle are pushed and the particles behind are drawn, so that the tagged particle move over long distances without collisions. Just above the melting point, it can be seen from Fig. 3 that the positions of the oscillations in the three simulated VACF do not match between each other and that their amplitudes are different. It is also evident that $\psi(t)$ coming from the EC(U2) model does not predict the monotonous decay at the lowest electron density, as observed for the two other models as well as in other works.[25,30] Incidentally, we have shown in Table II the self-diffusion coefficient D given by the area under the VACF curve. It should be noted that D is sensitive to the interionic potential used for simulation and that its density dependence is more important for the EC(U2) model than for the EC(I) model, respectively, 40 and 17 times between the two extreme densities. Compared with the MD predictions of Kahl,[24] the results obtained from the EC(I) model are in excellent concordance.

In short, the density dependence of the EC(U2) pseudopotential parameters appears to have an undesirable effect on the predicted behavior of expanded liquid metals. While the density dependence of the electron gas dielectric function seems to be satisfactory to describe the structural and dynamical properties along the liquid-vapor coexistence curve, its incorporation into the parameters of the EC pseudopotential leads to physically unacceptable features of the structure factor and VACF. In fact, the EC(U2) model should be able to predict these properties if an effective larger electron density was used in place of the true density. Intuitively, as the global volume of the fluid expands, it appears that the packing fraction of EC(U2) fluid remains constant, while it should decrease as it does for the two other models. This implies that the compressibility of EC(U2) does not increase quickly enough as can be assessed from the low-q limit of $S(q)$. This also explains the persistence of the oscillatory behavior of the VACF. These drawbacks do not appear with EC(I) and EC(U1) parameters, which are independent on the density.

Recently, Bermejo *et al.*[31] attempted to determine whether the success of an interionic potential could be attributed to other features than both the softness of the repulsive core and the oscillatory tail. In this respect, they consider as criterion to appreciate the reliability of a potential $u(r)$ the Grüneisen parameter under the simple form $\gamma_G = -(r_m/6)u'''(r_m)/u''(r_m)$, which is valuable if the nearest-neighbor interactions are only retained and where the primes stand for the derivatives of $u(r)$ at its minimum r_m. It can be seen from Table II that γ_G decreases with decreasing density for the EC(I) and EC(U1) models whereas it increases for the EC(U2) model. On the basis of our analysis, we believe that the discrepancies observed with the EC(U2) model are largely due to the specific variation of the packing fraction η of the system, whose an indicator given by $(\sigma/r_s)^3$ can be deduced from Table II. The density dependence of the two-parameters pseudopotential reveals an important increase of η when the density diminishes. It seems to us that the optimum behavior for liquid metals should be a more or less slow decrease of η with decreasing density, a situation met when the effect of the density is only taken into account in the dielectric function, as for the EC(I) and EC(U1) models. Thus, we expect that the variation of the parameters R and α with r_s is probably exaggerated in the case of the EC(U2) model, and that the first node of the interionic potential should scarcely move when the density varies. In this connection, it should be stressed that the energy dependent non local pseudopotential of Shaw has this particular characteristic.[25] Useful as it is for the calculation of the energetic properties of solids, the EC(U2) model is not the most appropriate one to investigate the structural properties of liquid metals. The drawbacks reported in this article in the case of rubidium have also been observed for other simple metals. The conclusion to be drawn from the results obtained in this work is that the density dependence of the electron gas dielectric function is crucial to yield quantitative prediction of the static and dynamic properties of expanded liquid metals. On the other hand, the dependence of the parameters of the EC pseudopotential seems rather prejudicial to this determination.

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