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Local field factor and effective potentials in liquid metals

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Abstract

The authors recently evaluated the local field factor, $G(q)$ of the electron gas by accurate fixed-node diffusion Monte Carlo (DMC) simulations. Here, the $G(q)$ obtained from a simple fit to the DMC results and from several approximations available in the literature is used to derive the effective pair potential $\phi(r)$ in simple metals within second-order perturbation theory. Using a local electron-ion pseudopotential, it is found that ϕ is determined mostly by the behavior of $G(q)$ at $q \leq$ ca. $2q_F$, where the DMC data are well reproduced by the local field within local density approximation, $G_{LDA}(q) = A(q/q_F)^2$ with A related to the compressibility of the uniform electron gas.

1. Introduction

The local field factor $G(q)$ is a convenient measure of exchange and correlation effects beyond the RPA in the problem of the linear screening of an external charge by the electron gas [1,2], which involves the dielectric function

$$\epsilon(q) = 1 - \frac{v_c(q)\chi_0(q)}{1 + v_c(q)G(q)\chi_0(q)}. \qquad (1)$$

Here, $v_c(q) = 4\pi e^2/q^2$ is the Coulomb coupling and $\chi_0(q)$ the response function of non-interacting electrons. Evidently, $G(q) = 0$ yields the RPA, $\epsilon_{RPA}(q) = 1 - v(q)\chi_0(q)$. Over the years many approximations have been developed for $G(q)$, their accuracy being indirectly tested [1,2] through the predictions of quantities such as correlation energy and pair correlation functions. Only recently computer simulations of the dielectric screening in the electron gas have been performed, in two [3] and in three dimensions [4,5], yielding very accurate information on $G(q)$.

The $G(q)$ of a many-electron system is important in crucial problems. It provides information on the exchange-correlation functional $E_{xc}[n]$ of density functional theory [6], which is widely applied in the study of real materials [7]. Moreover, it is a basic ingredient of the pseudopotential perturbation treatment of simple metals [8,9], in that it directly determines the effective inter-ionic pair potential $\phi(r)$ [9]. Here we assess the dependence of $\phi(r)$ on the choice of the local field, taking as reference our diffusion Monte Carlo (DMC) predictions, which may be considered the most accurate to date. We restrict this preliminary analysis to the very simple empty core pseudopotential (ECP) of Ashcroft [10].

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2. Results

2.1. Local field factor of the electron gas

Calculating the static response of a quantum fluid with numerical simulations is straightforward [3,5]. One perturbs the otherwise homogeneous many-body system with a static external potential

$$v_{\mathrm{ext}}(\boldsymbol{r}) = 2v_q \cos(\boldsymbol{q}\boldsymbol{r}), \tag{2}$$

which induces a modulation of the density with respect to its mean value n_0 and a shift of the ground state energy (per particle) [3]

$$E_v = E_0 + \frac{\chi(q)}{n_0} v_q^2 + \frac{\chi^{(3)}(\boldsymbol{q},\boldsymbol{q},-\boldsymbol{q})}{4n_0} v_q^4 + \cdots, \tag{3}$$

with $\chi(q)$ and $\chi^{(3)}$ the linear and cubic response functions. DMC allows an accurate evaluation of E_v for given $\boldsymbol{q}$ and v_q. By performing simulations at few coupling strengths v_q one can extract $\chi(q)$ as well as higher order response functions from the calculated E_v, by fitting in powers of v_q. Clearly the procedure must be repeated for each value of the wavevector and of any other relevant parameter characterizing the system, which makes it somewhat demanding computationally.

$G(q)$ is immediately extracted from the computed $\chi(q)$ by combining Eq. (1) with the exact relation $1/\epsilon(q) = 1 + v_c(q)\chi(q)$, which yields

$$v_c(q)G(q) = \chi^{-1}(q) - \chi_0^{-1}(q) + v_c(q). \tag{4}$$

In Fig. 1 we show our results [5] for a density close to that of aluminum, $r_s = 2$, where r_s is defined by $n_0 = 1/(4\pi r_s^3 a_B^3/3)$ and n_0 and a_B are the number density of the homogeneous electron gas and the Bohr radius, respectively. It is evident that the DMC results smoothly interpolate between the known small and large q behavior, which are also shown. Thus they may be fitted to a simple formula [5], embodying independent information on the uniform electron gas. Most of the available approximations [1,2] would give a $G(q)$ saturating to a constant at large q, which has been shown to be wrong [13]. In Fig. 1, we also show the prediction of the only two interpolation schemes [11,12] to date that reproduce the correct asymptotes of the local field. Note that the small q behavior (given by the dashed parabola) extended to all values of q corresponds to the local density approximation (LDA) prediction.

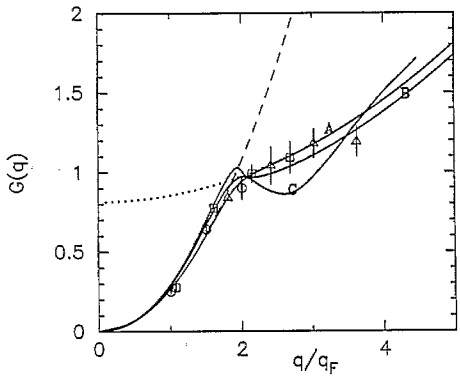

Fig. 1. Electron gas $G(q)$ at $r_s = 2$. Symbols give DMC results [5] and the dashed and dotted parabolas the small and large q behavior. Curves A, B and C give an interpolation of the calculated points [5] and the predictions of [11] and [12].

2.2. Effective pair potentials

Linear screening theory in its simplest formulation leads [9] to the following expression for the Fourier transform of the effective ion–ion interaction in simple metals:

$$\phi(q) = \frac{4\pi Z^2 e^2}{q^2}\left(1 + \left(\frac{1}{\epsilon(q)} - 1\right)\left(\frac{V_p(q)q^2}{4\pi Ze^2}\right)^2\right), \tag{5}$$

where Z is the valence of the metal ion and $V_p(q)$ a local, energy independent electron–ion pseudopotential. Here we restrict ourselves to the simple Ashcroft pseudopotential [10]

$$V_p(q) = -\frac{4\pi Ze^2}{q^2}\cos(qr_c), \tag{6}$$

which is specified by one parameter, the core radius r_c, but gives a fair description of a number of properties of simple metals [9].

We consider in detail Na and Al at their freezing densities, using the local field factor fitted to our DMC results [5] as well as those due to (i) Singwi, Sjölander, Tosi, and Land (SSTL) [14], (ii) Vashista and Singwi (VS) [15], (iii) Ichimaru and Utsumi (IU)

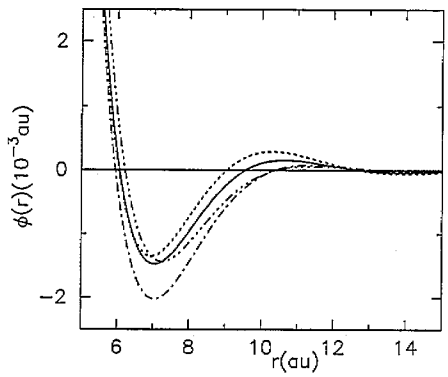

Fig. 2. Effective pair potential of Na at freezing, with $r_c = 1.69$ au, for several choices of $G(q)$. Full and dashed curves (which coincide): fit to DMC results and LDA; dash–dot and dash–dot–dot curves: VS [15] and SSTL [14]; dotted curves (which coincide): IU [16], FHER [11].

[16], (iv) Farid, Heine, Engel and Robertson (FHER) [11], and (v) the one resulting [5] from the LDA. We fixed the core radius r_c to 1.69 au for Na and 1.12 au for Al, values which yield a satisfactory description of phonon dispersion in the crystalline phase of these materials [17,18].

In Fig. 2 we show the effective pair potential in liquid Na at freezing ($r_s = 4.05$). With the exception of the VS, the various local fields all yield a potential well of about 1.4 mH at $r \simeq 7$ au, though moderate differences remain in the shape and location of the well. The VS, instead, yields a deeper well of about 2 mH. We note that the predictions of DMC and LDA, on the one hand, and those of the IU and FHER approximations, on the other, are completely equivalent in this case.

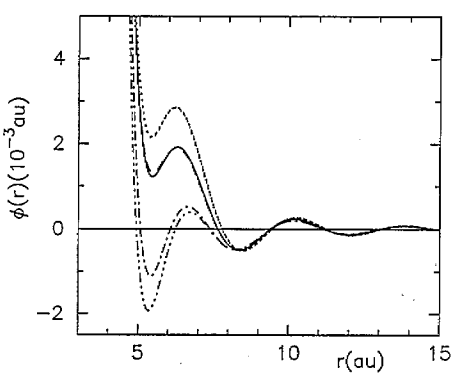

Fig. 3. Effective pair potential of Al at freezing, with $r_c = 1.12$ au, for several choices of $G(q)$. Notation as in Fig. (2).

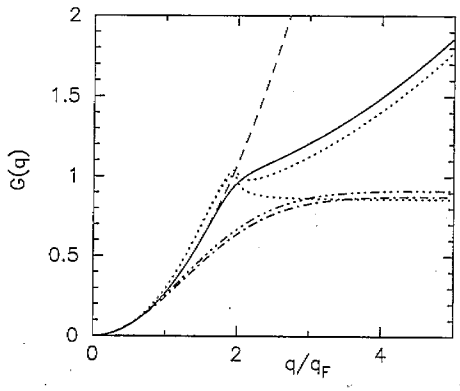

Fig. 4. Electron gas $G(q)$ at the density of Al at freezing, $r_s = 2.16$. Notation as in Fig. (2). Upper and lower dotted curves give the approximations of FHER [11] and IU [16], respectively.

In Fig. 3, we show the pair potentials for Al at freezing ($r_s = 2.16$). Also in this case, there is a substantial equivalence of the prediction of DMC and LDA, on one hand, and of IU and FHER approximations, on the other. However for the polyvalent Al, there is much more spread in the results. At distances $r \simeq 5.3$ au one finds a deep well from SSTL, a shallower one from VS and a shoulder at different height for DMC/LDA and IU/FHER. In Fig. 4, we report the various local fields used for Al. It is evident that local fields which are similar below $2q_F$, such as DMC/LDA and IU/FHER, yield equivalent predictions for $\phi(r)$, even though they depart considerably from each other above $2q_F$.

3. Conclusions

Through the use of DMC results for $G(q)$ and local pseudopotentials, we have established that an accurate knowledge of the local field is especially important for wavevectors below $2q_F$ in the construction of effective pair potentials. Details of $G(q)$ at larger wavevectors, on the other hand, seem to be unimportant. Thus the popular approximation of Ichimaru and Utsumi [16] appears to be equivalent to that of Farid et al. [11], though the latter is much more precise at large q. At any rate, both yield pair potentials at variance with the prediction from DMC. We find that the predictions obtained from our fit [5] to the DMC local field are almost equivalent to those from the LDA local field [5], and thus either scheme

should be preferred to the other approximations available to date. It remains to be seen if similar conclusions may be extended to the case of non-local energy-dependent pseudopotentials, which are essential if one has to go beyond the simple sp-bonded metals.

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