

Density-Functional Study of C, Si, and Ge Metallic Liquids

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A density-functional study of C, Si, and Ge metallic liquids is reported. Pair potentials are constructed from pseudopotentials which reproduce the Kohn-Sham densities. These lead to structure factors $S(k)$ in good agreement with experiment, and with more elaborate Car-Parrinello calculations. It is predicted that liquid carbon has a single sp band, is highly conducting and strongly compressible, with a broad peak in $S(k)$ located near the "hump" in the $S(k)$ of l -Si.

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Liquid C, Si, and Ge have recently attracted much attention¹⁻³ and liquid carbon (l -C) is found to have an electrical resistivity similar to l -Al.⁴ The vapor phases contain covalent clusters, as for most metals. Solid C, Si, and Ge are insulators or semiconductors with covalent bonding. The increase in density of Ge and Si on melting favors the transition from covalency to metallicity. However, the coordination numbers ($\sim 6,7$) for l -Si and z -Ge are low compared to $\sim 10,12$ found in most liquid metals. The structure factors $S(k)$ of Si and Ge are also unusual^{3,5} in having a main peak of height ~ 1.5 compared to, say, ~ 2 in most metals, together with a hump (shoulder) on the high- k side of the main peak, at $k \sim 1.8$ a.u.⁻¹. Many authors have considered these to be signatures of covalent structures persisting in the fluid. Ashcroft² has argued that a consistent picture of the $S(k)$ of l -Ge could be constructed even from an extreme model where the fluid is assumed to contain transient Ge_4 clusters with fast exchange, rather than individual Ge^{4+} ions, while suggesting that the actual situation may be somewhere in between this limit and a model of diffusively free ions. In Ashcroft's picture, the shoulder in $S(k)$ is mainly a manifestation of the internal modes of Ge_4 , while the main peak arises from a synthesis of hard-sphere-type correlations among the Ge_4 clusters and the internal cluster structure. Recent Car-Parrinello- (CP-) type molecular-dynamics (MD) studies¹ support the existence of such transient structures involving several ions. However, a systematic study of a simple-metallic model for C, Si, and Ge is of interest.

In this Letter we report a study of l -C, l -Si, and l -Ge using density-functional theory (DFT) within the local-density approximation (LDA), using approaches valid for simple metals and plasmas. In the spirit of DFT we assume that the displaced electron density $\Delta n(r)$, or its Fourier transform $\Delta n(q)$, due to an ion in jellium determines the pseudopotential $V_{ie}(q)$. This V_{ie} and the electron-gas response function $\chi(q, r_s)$ define a "second-order" pair potential $U(q)$ valid in the linear response (LR) regime. The pair potential can be used in MD or

in an integral equation, e.g., the modified hypernetted chain (MHNC) equation,⁶ to generate the $S(k)$ and the pair function $g(r)$ of the fluid. Figure 1 shows the results of such calculations for liquid C, Si, and Ge. The calculations for carbon were at a density 2.0 g/cm³ (Wigner-Seitz radius $r_{WS} = 2.5236$ a.u., electron sphere radius $r_s = 1.5898$ a.u., and temperature $T = 5000$ K). Liquid Ge with $r_{WS} = 3.2703$ a.u., $r_s = 2.0602$ a.u., and $T = 1256$ K, and liquid Si with $r_{WS} = 3.0727$ a.u., $r_s = 1.9357$ a.u., and $T = 1733$ K are at their melting points. Figure 1 shows theoretical curves for C, Si, and Ge and Salmon's³ neutron data for $S(k)$ of Ge. The high- k shoulder at $k \approx 1.8$ a.u.⁻¹ in l -Ge becomes more pronounced in l -Si and finally becomes the main peak in the $S(k)$ of l -C. The broad first peak in the $S(k)$ of carbon corresponds to a narrow peak in the $g(r)$, where the first and second maxima occur at 2.6 and 5.2 a.u., in good accord with the MD results of Galli *et al.*¹

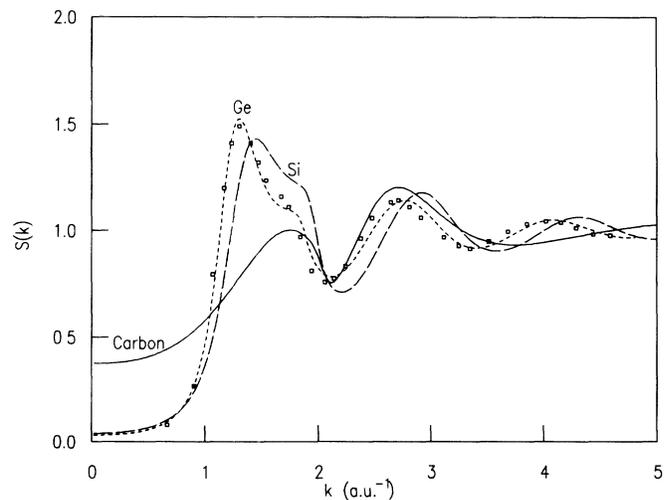


FIG. 1. Calculated $S(k)$ of l -C, l -Si, and l -Ge. Squares: Salmon's (Ref. 3) experimental $S(k)$ for l -Ge.

The DFT $\Delta n(q)$ is calculated via a construction of the neutral pseudoatom for the ion in a cavity embedded in jellium.⁷ However, unlike in a CP calculation,¹ only a single-center radial Kohn-Sham equation is solved. Thus multi-ion effects are neglected. Figure 2 shows the displaced density $\Delta n(q)$ calculated from LDA DFT for carbon and silicon. Ge^{4+} is similar to Si^{4+} , and is not shown. The DFT $\Delta n(q)$ for both Si^{4+} and Ge^{4+} (but not C^{4+}) can be modeled quite well by the LR form $\Delta n(q) = -ZV_q \cos(qR_0)\chi(q, r_s)$, where atomic units are $e = \hbar = m_e = 1$, and $V_q = 4\pi/q^2$, $Z=4$. $\chi(q, r_s)$ contains the LDA local-field correction $G(q, r_s)$. The empty-core pseudopotential $V_{ie}(q) = -ZV_q \cos(qR_0)$, and contains the radius R_0 determined by fitting to the DFT $\Delta n(q)$. The pair potential $U(q)$ is $Z^2V_q - V_{ie}(q)^2\chi(q)$. Previous work⁸ has shown that l -Ge can be extremely well modeled with such a simple V_{ie} and an effective response function $\chi(q, r_s^*)$ evaluated at the effective density parameter r_s^* , with the effective mass $m^* = r_s^*/r_s \approx 1$ (full definitions of functions with r_s^* are given in Ref. 9). Figure 2 shows, for Si, the simplest "nonoptimized" LR description (squares) where $m^* = 1$ and R_0 is determined from the first zero in the DFT $\Delta n(q)$. Comparison with the DFT $\Delta n(q)$ shows that even the "nonoptimized" description is quite good and LR is valid for Si.

A simple way⁷ of constructing a pseudopotential from $\Delta n(q)$ is to define an effective linear pseudopotential $W(q) = \Delta n(q)/\chi(q)$. This uses the full information contained in the DFT $\Delta n(q)$ rather than the part of $\Delta n(q)$ consistent with a given fitting model. Both $W(q)$ and $V_{ie}(q)$ lead to similar results in the linear regime. In fact, the theoretical $S(k)$ for Si shown in Fig. 1 was ob-

tained from a $U(q)$ constructed from $W(q)$.

The DFT $\Delta n(r)$ for C^{4+} is different from those of Ge^{4+} and Si^{4+} , owing to the very small core size of C^{4+} . The DFT $\Delta n(r)$ of C contains an s ($l=0$) and a p ($l=1$) component. LR is not expected to be valid *a priori* in this case. The linear pseudopotential $W(q)$ defined from the DFT $\Delta n(q)$ of C^{4+} changes character sharply near $2k_F$, unlike in Si or Ge. This suggests that more elaborate forms of V_{ie} (e.g., nonlocal forms, etc.) would perhaps be useless. Density-of-states calculations for C^{4+} (see below) show that carbon has a *single sp band*. Hence we assume that the nonlinearity of the electron response rather than the nature of the pseudopotential is most crucial. To support this, Fig. 2 shows that the DFT $\Delta n(q)$ of C^{4+} , viz., $\Delta n_C(q)$, is very similar to $\Delta n_{\text{Si}}(q)$ in that $\Delta n_{\text{Si}}(q)$ can be trivially scaled to give $\Delta n_C(q)$ by replacing q by fq , $f \sim 1.55$, for $q < 2k_F$. Thus for small q , the typical momentum scales of the problem are redefined while the electron-ion interactions in l -C remain similar to those of Si^{4+} and Ge^{4+} . Thus we expect the simple V_{ie} to work even in the case of C^{4+} but with a $\chi(q^*, r_s^*)$ containing r_s^* and a q^* reflecting the change of q scales. In effect, the electron gas in l -C behaves, for small q , i.e., for long-range interactions, as if its effective density were *lower* than the nominal density. The triangles in Fig. 2 show the $\Delta n(q)$ for C^{4+} calculated from V_{ie} and a scaled $\chi(q^*, r_s^*)$, obtained by optimizing R_0 , m^* , and f such that $q^* = fq$ to fit the DFT $\Delta n(q)$. The values of R_0 , m^* , and f were 0.3672 a.u., 1.6585, and 1.1758, respectively. This three-parameter description of the DFT $\Delta n(q)$ reproduces the DFT density *not only in q space, but also in r space* (inset of Fig. 2). Of course, very-large- q or very-small- r (core) regions are not fitted. The results shown in Fig. 2 imply that the DFT $\Delta n(q)$ of C^{4+} can be represented by a quasilinear response (QLR) form although standard LR fails. Given the stringency of the requirement that the charge densities in q space and in r space have to be recovered to high accuracy, we believe that the present approach to modeling the DFT charge density is not just an arbitrary procedure, but a meaningful generalization of the LR approach.

The pair potentials $U(r)$ are shown in Fig. 3(a). In Ge we have included a core-core polarization term $\Delta U(r)_p = -0.75\omega_0 a^2(0)/|r^2 + r_c^2|^3$, where $\omega_0 = 1.22$ a.u. and $\alpha = 6.748$ a.u.³ A cutoff radius r_c was used and $\Delta U(r)_p$ was verified to be independent of r_c for $r_c/r_{\text{WS}} = 1.0$ or $r_c/r_{\text{WS}} = 0.5$. The core-polarization term has the effect of *slightly* increasing the main peak in the $S(k)$ of Ge. Figure 3(a) shows that the pair potentials of C, Si, and Ge are very similar except for the very small core size of C^{4+} , defined by the steep wall of the C-C potential. Figures 3(b) and 3(c) compare the Ge^{4+} pair potential with the Dagens, Rasolt, and Taylor¹⁰ (DRT) potential for l -Al near the melting point for which $r_{\text{WS}} = 3.121$ a.u., $r_s = 2.164$ a.u., $Z = 3$ and which resembles l -Ge ($r_{\text{WS}} = 3.27$, $r_s = 2.06$, $Z = 4$). The DRT

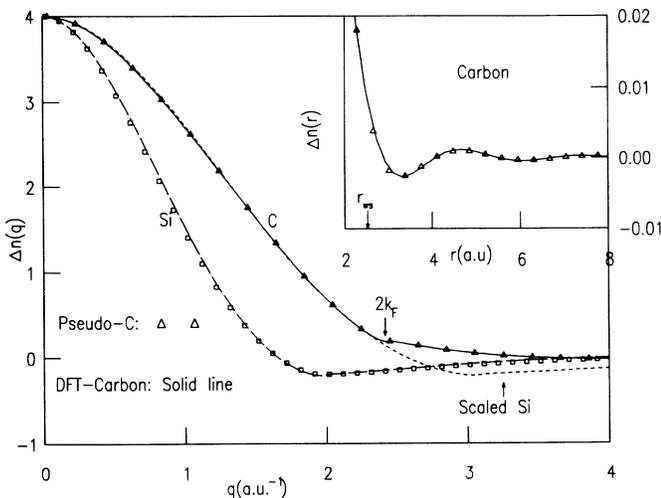


FIG. 2. The DFT $\Delta n(q)$ for Si^{4+} and C^{4+} are compared with pseudopotential predictions. Squares: LR $\Delta n(q)$ for Si with $R_0/r_{\text{WS}} = 0.3084$. The curve "scaled Si" shows that the $\Delta n(q)$ of Si can be simply scaled to give the $\Delta n(q)$ of C for $q < 2k_F$. Triangles: QLR $\Delta n(q)$ for pseudo-carbon. Inset: DFT $\Delta n(r)$ and QLR $\Delta n(r)$ in r space for carbon.

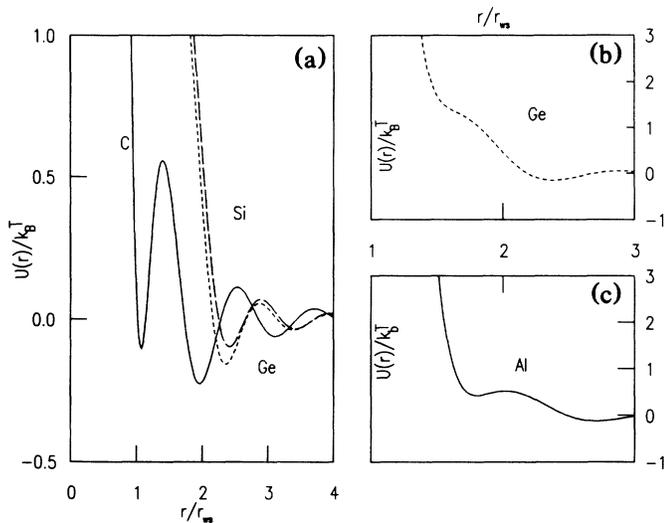


FIG. 3. (a) Pair potentials for liquid C, Si, and Ge at 5000, 1733, and 1256 K, respectively. (b),(c) Comparison of the Ge pair potential with the DRT potential of *l*-Al.

pair potential has a positive ledge of about $0.5k_B T$ near $r/r_{WS} \sim 2.0$, and a negative minimum of about $0.15k_B T$ near $r/r_{WS} = 2.7$. The positive ledge at $0.5k_B T$, $r/r_{WS} \sim 2$ defines the first-neighbor position and the Al $S(k)$ shows a single maximum near $kr_{WS} \sim 4.5$. In the $U(r)$ of *l*-Ge we have, as in Al, a ledge but at about $2k_B T$ near $r/r_{WS} \sim 2$, and a negative minimum of $0.15k_B T$ near $r/r_{WS} \sim 2.3$. Unlike in Al, the competing negative minimum and the positive ledge lead to a weakened maximum in $S(k)$ of Ge at $kr_{WS} \sim 4$ and a hump, arising from the positive ledge, at $kr_{WS} \sim 5.5$. The splitting of the ions between two locations reduces the coordination number from the usual $\sim 10, 11$ (as in Al) to the $\sim 6, 7$ found from the area under the first peak in the $g(r)$ of Ge^{4+} . The main peak in $S(k)$ of *l*-C is broad and it arises from the sharp Friedel oscillation at $r \sim r_{WS}$. The calculated $S(k \rightarrow 0)$ implies that *l*-C is highly compressible since $S(0)$ is ~ 0.36 compared with ~ 0.03 for *l*-Si. Hence a measurement of the compressibility of *l*-C would be very useful. The predicted high compressibility of *l*-C needs comment since *l*-C is a liquid with an $r_s \approx 1.6$. It was shown that the *electron response* behaved with an $r_s^* \approx 2.64$. Further, the hard wall of the C-C potential occurs (Fig. 3) at $r = r_{WS}$ and hence the equivalent hard-sphere liquid has a packing fraction $\eta \approx 0.1$ and a compressibility very close to our $S(0)$.

$S(k)$ for *l*-Si calculated using the MHNC equation⁶ agrees quite well (Fig. 4) with the MD results of Ref. 1(b), and both agree with x-ray data⁵ to about the same extent. The long-dashed curve shows the $S(k)$ obtained using the Stillinger-Weber¹¹ (SW) potential containing two-body and three-body terms, and cut off to zero between the first- and second-neighbor distances. The pair potentials used by us are by contrast very long ranged, as

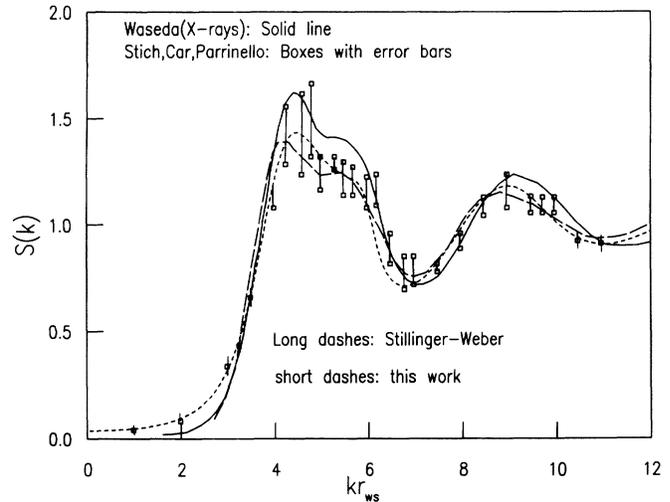


FIG. 4. Calculated $S(k)$ of *l*-Si compared with the MD results of Ref. 1(b), Ref. 11, and x-ray data (Ref. 5). The MD points were obtained by enlarging Fig. 1(a) of Ref. 1(b) and Fig. 6 of Ref. 11.

dictated by the physics of Friedel oscillations in an electron gas. SW-type potentials^{11,12} have a phenomenological form with many parameters fitted to theoretical overlaps, bonding energies, and structural properties. Biswas and Hamann¹² use eighteen parameters, and the SW potential has eight parameters, while the Si potential used for the $S(k)$ of this work has no adjustable parameters, but is specific to the density and the material. Unlike in our "metal physics" approach, the method of Refs. 11 and 12 deliberately ignores the structure-independent form of the "electron-gas" term in the total energy E and fits E to a many-body potential which is short ranged by choice. The diamondlike structure typical of C, Si, and Ge is not stable under short-range forces and many-body terms are needed in short-range interaction models. While these short-ranged many-body potentials have their merits, e.g., in simulations, so far the errors, even in properties which depend on mere quadratic displacements from equilibrium, like the elastic constants (30% error with SW for Si) and the optical-phonon frequency (17% error), tend to be too high.¹³ However, the many-body-potential concept is closer to the transient cluster picture. Contour plots of electron density in *l*-Si shown in Ref. 1 are suggestive of transient covalent bonds. It is likely that a CP-type MD study of *l*-Al might lead to similar plots, although *l*-Al is hardly considered as a fluid containing transient covalent clusters.

The nonlinear electron response in C implies that the displaced charge density near two C ions would not be the simple superposition of individual charge densities. Such a superposition assumption is implicit in the scaled QLR model used here. A quantitative picture of the inadequacies of the single-center calculation is obtained from Fig. 5 where the density of states $N(\epsilon)$ obtained (from the DFT phase shifts) is compared with that of

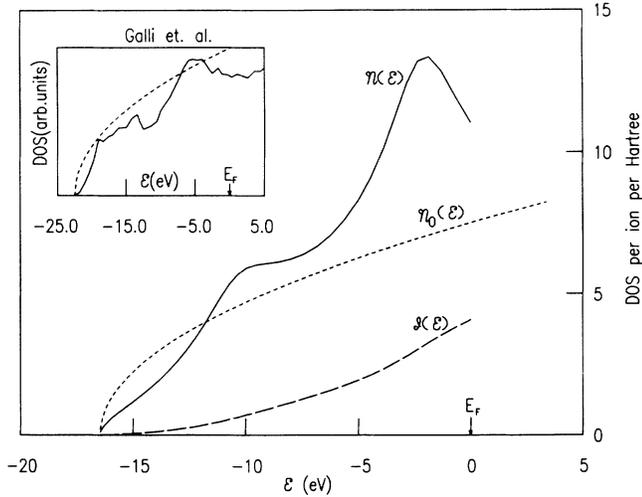


FIG. 5. The electron density of states $N(\epsilon)$ in l -C calculated from the DFT phase shifts. Short-dashed line: The free density of states $N_0(\epsilon)$. The integrated density of states $I(\epsilon)$ is 4 at the Fermi energy E_F . Inset: CP MD results for Galli *et al.* (Ref. 1).

Galli *et al.*¹ Both calculations show that l -C has a single sp band. The stronger localization of electrons found in the MD calculation of Galli *et al.*¹ is also reflected in the $g(r)$. Although our peak positions and the height of the second peak of the $g(r)$ of carbon are in good accord with Galli *et al.*, our first-peak height (~ 1.6) is low compared to that of Galli *et al.* (~ 2.3). The first peak in the $S(k)$ of carbon shown in Fig. 1 is likely to be enhanced if short-range correlations underestimated by the present one-center model could be included.

Using the V_{ie} , χ , and $S(k)$ derived from them using the MHNC equation, the electrical resistivities ρ can be calculated from the Ziman formula. We obtain 80.6, 22.7, and 28.4 $\mu\Omega$ cm for the resistivity of C, Si, and Ge liquids, to be compared with the experimental values of 30–70 $\mu\Omega$ cm reported⁴ for l -C and 80.6 and 70 $\mu\Omega$ cm for l -Si and l -Ge, respectively.¹⁴ The underestimate in ρ for Si and Ge is similar to that of Ashcroft and Lekner.¹⁵ We pointed out that in Si and Ge, unlike in Al, the coordination shell is split between two competing sites. Thus additional scattering effects would be important in l -Si and l -Ge. Further, Fig. 5 shows that the one-center model for l -C underestimates electron localization in comparison to Galli *et al.* The CP-type calculations¹ give a ρ of 57–120 for l -Si and 140 ± 28 $\mu\Omega$ cm for l -C and seemingly overestimate electron localization.

In summary, we have shown that the static structural aspects of both liquid Si and liquid Ge can be described quite well by very simple pseudopotentials and response functions. In l -C the nonlinear electron response could

be modeled by a simple quasilinear form. We predict that l -C is a highly compressible liquid with a weak broad first peak in $S(k)$ near 1.76 a.u.⁻¹ and a stronger peak near 2.7 a.u.⁻¹.

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