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# Simulations of liquid semiconductors using quantum forces

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We present results for the structural and electronic properties of liquid Si and Ge using *ab initio* molecular dynamics. The interatomic forces are calculated from *ab initio* pseudopotentials constructed within the local-density approximation. The simulations do not utilize fictitious electron dynamics; the system is constrained to reside on the Born-Oppenheimer surface at each step of the simulation. Langevin dynamics are used to control the temperature of the system. Predicted pair and angular correlation functions, structure factors, and self-diffusion coefficients are presented for both Si and Ge.

## I. INTRODUCTION

The liquid state ($l$ state) of matter presents formidable challenges in the application of theoretical methods for predicting electronic and structural properties. For example, semiconductors such as Si and Ge, have been extensively studied in the crystalline phase, but the liquid properties for these semiconductors have not received similar attention. Although $l$-state Si and Ge are technologically important (e.g., zone refining in laser annealed surfaces or crystal growth), the high melting points, 1693 K for Si and 1210 K for Ge, and high reactivity of these liquids make experimental examinations difficult.[1]

Theoretical studies of liquid Si and Ge have also been somewhat limited. Dynamics play a crucial role in determining the properties of the liquid state. Unlike the solid state, a key issue in modeling the liquid state is constructing a representative ensemble. The crystalline form of Si and Ge is covalent, and corresponds to the diamond structure. This is an open structure with a coordination number of 4. Open structures cannot be reproduced by simple pairwise interactions. In the solid state, *many-body* interatomic potentials are required to replicate the diamond structure. Although the coordination number increases upon the solid → liquid transition to $\sim 6$, and the conductivity jumps by a factor of 20 for Si and 11 for Ge, there are indications that the materials do not have entirely free-electron character, but still retain *covalent* properties.[1]

For example, $l$ structures of Si and Ge remain somewhat "open" if we compare[2] with close-packed liquid metals with coordination number $\sim 12$. Also, liquid Si and Ge structures differ from simple metals in terms of long-range correlations.[3] These attributes of Si and Ge make it very difficult, if not impossible, to simulate the $l$ state using simple pairwise atomic potentials, or by using a model based on the packing of hard spheres. In this sense, the best approach to calculating the properties of liquid Si and Ge (or other covalent liquids) would be to utilize fully quantum-mechanical methods.

Only recently has it been possible to apply quantum methods to complex systems such as liquids. Early theoretical studies attempted to use empirical, many-body interatomic potentials, or semiempirical approximations.[4–7] More recent methods have focused on *ab initio* calculations. These calculations have become feasible owing both to hardware developments, e.g., parallel computers, and to software developments, e.g., new algorithms. An example of an algorithm development is the *ab initio* method in the work of Car and Parrinello.[8] Their approach can be applied to complex systems, and has been used to examine semiconductor liquids. The Car-Parrinello method uses *fictitious dynamics* for the electrons and *Newtonian dynamics* for the ions, simultaneously minimizing the energy with respect to the electronic and ionic degrees of freedom. However, it is *not* necessary to employ fictitious electron dynamics to achieve an efficient simulation procedure.[9–13]

We introduce a different approach from the Car-Parrinello method.[9,10] As in their method, we use *ab initio* pseudopotentials to compute quantum interatomic forces which are then incorporated into a dynamical simulation. In contrast to the Car-Parrinello method, we do not involve fictitious "electronic degrees of freedom." We restrict our simulation to reside on the Born-Oppenheimer surface. This procedure allows us to take much longer steps in integrating the equations of motion. The longer time steps compensate for performing a fully self-consistent calculation, and implementing the *real* quantum forces, at each time step.

Our simulations also differ from previous *ab initio* calculations in the way we thermalize the liquid system. We use Langevin dynamics[13,14] rather than Nosé[15] dynamics. In Langevin dynamics, particles are subject to random fluctuative and dissipative forces which simulate a coupling to a heat bath. The work imparted to the system by the random forces is dissipated by the viscous forces from the hypothetical medium. Since we are not only interested in statistical properties, but also in the dynamical behavior of the system, we adopt the following strategy. Once the desired equilibrium temperature is achieved by Langevin thermalization, the viscosity of the hypothetical medium is reduced to zero. The *canonical ensemble* from the Langevin simulation is thus converted into a *microcanonical ensemble* with the desired temperature. With the temperature of interest established, we can then follow the dynamical behavior of the liquid.

We apply this method to compute the properties of liquid Si and Ge. We calculate the pair-correlation functions, the angular distribution functions, the structure factors, the self-diffusion coefficients, and the coordination numbers. We compare our calculations to previous theoretical results, and to experimental data, where available.

## II. COMPUTATIONAL METHODS

A key aspect of simulating a liquid is preparing a representative ensemble. We started our simulation with 64 atom supercells for both Si and Ge. Studies using realistic interatomic potentials[16] have suggested that a 64-atom system is sufficiently large to capture the essential features. In the case of Si, we prepared the liquid state by first arranging the atoms in *crystalline* Si configuration and then heating it. The size of the cell was taken in such a way that it corresponds to a cubic diamond unit cell with a doubled lattice constant, $2a$. The size of the cell for Si was taken to be 10.48 Å. This cell size corresponds to the known experimental density of the liquid near the melting point. The densities of Si and Ge are greater than densities of solid phases by 10 and 4 %, respectively.[1]

To avoid any "memory" or hysteresis effects, we start the systems far above the melting point and anneal the systems to just above the melting point temperature. This procedure has been used elsewhere.[3,17,18] For Ge, we proceeded in a similar manner. However, we started the simulation from a random configuration of Ge atoms in the supercell. This procedure is probably superior in that the initial random state is closer to a liquid state. As for Si, we determine the supercell size for the Ge $l$ state by fixing the density to correspond to the experimental value. The lattice constant for the Ge cell was taken to be 11.24 Å. Again, the initial temperature was taken to be well above the known melting point of Ge.

In our simulation, the trajectory of each silicon or germanium atom is computed from the Langevin equation:

$$M_i \frac{d\mathbf{v}_i}{dt} = -\gamma \mathbf{v}_i + \mathbf{F}_i + \mathbf{G}_i(T), \tag{1}$$

where $\mathbf{F}_i$ is the interatomic force on $i$th particle, $M_i$ is the mass of Si or Ge, and $\gamma$ is the viscosity of the hypothetical medium. The temperature of the medium is taken to be $T$. The particles are subject to rapidly varying random forces $\mathbf{G}_i$. The random forces, temperature, and viscosity are interrelated by the fluctuation-dissipation theorem.[19] The interatomic forces $\mathbf{F}_i$ are computed quantum mechanically from *ab initio* pseudopotentials with a plane-wave basis set.[9] Pseudopotentials were constructed in the Troullier and Martins[20] form with the Ceperley and Adler[21] form for correlation. Cutoff radii were $r_c = 2.50$ for Si and $r_c = 2.68$ for Ge. We used a plane-wave cutoff of 8 Ry, and tested higher cutoffs. This cutoff is probably the smallest cutoff which one can employ, and still maintain accurate dynamics. A Kleinman and Bylander[22] factorized form for the pseudopotential was used. For Si, the form of the pseudopotential consisted of three angular projectors, with $s$ and $d$ nonlocal components. The local part of the pseudopotential was taken to be the $p$ component. For Ge the form had four angular projectors, with $s$, $p$, and $d$ nonlocal components. The local part was taken to be the $f$ component. This choice for Ge avoids problems associated with "ghost states."[23] The Brillouin zone was sampled only by the $\Gamma$ point. While the use of only one $\mathbf{k}$ point has been questioned[3] for determining the electronic density of states, it appears to be satisfactory for other properties such as the charge density, and for dynamical properties. We use a modified Beeman algorithm to integrate the equation of motion.[14]

A Broyden procedure was used to iterate the potential to self-consistency.[24] Our criterion for self-consistency requires the rms error of the "input" and "output" potentials to be less than $10^{-4}$ a.u. Typically, 5–6 iterations were required. The charge density from the previous time step was used to construct a starting potential. An iterative diagonalization procedure[25] was used to obtain the eigenvalue/eigenvector pair. The eigenvalues were converged to $10^{-7}$ a.u.

The initial temperature of the medium for both Si and Ge was taken to be 6000 K. In atomic units, the viscosity parameter $\gamma$ was taken to be 0.001 and the time step $\Delta t$ to be 250. The initial state was quenched rapidly to just above the melting point. For Si we took 240 time steps, or 1.4 ps, to reach 1800 K. For Ge we used a slower quench, i.e., 440 time steps, or 2.6 ps, to reach 1350 K. In our silicon simulation, the system was thermalized to the initial temperature of 6000 K in ~50 steps. The temperature of the system is taken from the kinetic energy of the atoms. For the germanium simulation, the system was equilibrated to the initial temperature within 10 time steps owing to the initial random configuration (which is more representative of a higher-temperature state). In both cases, the Langevin method provides an effective and convenient thermalization procedure. This method does not require any *ad hoc* rescaling of the particle velocities, or the use of Nosé dynamics.

In order to ensure the correct *dynamical* behavior of the liquid, once we have reached the desired temperature, we slowly decrease the viscosity to zero. At zero viscosity, the random forces must also vanish due to the fluctuation-dissipation theorem, and the system is transformed to a *microcanonical* ensemble. We then follow the trajectories of the particles to examine the liquid-state dynamics. Since the atoms of Ge are heavier than the atoms of Si and thus diffuse more slowly, we take more time steps for the simulation of liquid Ge than for liquid Si. With the temperatures established at 1800 K for Si, and 1350 K for Ge, the viscosity parameter was lowered by a factor of 2 for every 10 time steps for a total period of 40 steps for Si, and for every 20 time steps for a total period of 80 steps for Ge. At the final step, the viscosity was reduced to zero. We also shorten the time step $\Delta t$ in order to insure accurate dynamics. During the Langevin thermalization process, energy is not conserved and small errors in the dynamics can be tolerated. After turning the Langevin dynamics off, the rms error in the energy conservation was approximately $10^{-4}$ eV/atom. The drift in the total energy over the simulation time (~1 ps) was less than 0.01 eV/atom.

The system of $l$-Si was examined for 240 time steps (1 ps) and the system of $l$-Ge was examined for 300 time steps (1.2 ps). These simulation times should be satisfactory for obtain-

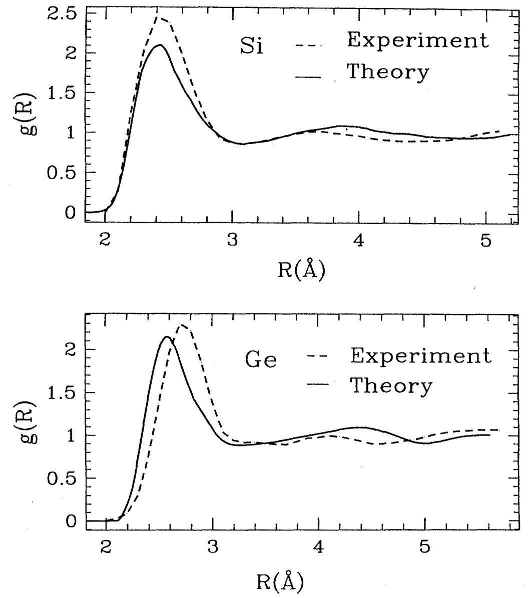

FIG. 1. Theoretical (solid line) and experimental (dashed line) pair correlation functions, $g(R)$, for Si and Ge.

ing an accurate description of the pair-correlation function, the structure factor, and the angular distribution functions. For example, work using tight-binding molecular dynamics for semiconductor liquids indicates that diffusion properties can be determined on such short time scales.[6]

In a microcanonical ensemble, the energy should be rigorously conserved. However, owing to the small size of the system, there are fluctuations of the kinetic energy. Our calculated rms fluctuation of the kinetic energy was about ~150 K for Si and ~100 K for Ge. The temperature as determined from the kinetic energy averaged over the simulation time was within a few percent of the desired temperature as fixed in the Langevin equation. This confirms the utility of Langevin procedure for establishing the desired temperature.

## III. THE STRUCTURAL PROPERTIES OF LIQUID SILICON AND GERMANIUM

A key measure of a liquid state is the pair-correlation function, or the radial distribution function. This quantity characterizes the structural properties of a liquid in an average sense. In Fig. 1, we show the calculated pair-correlation functions for Si and Ge. The pair-correlation functions were obtained by averaging over the liquid structure at different times during the microcanonical (zero viscosity) simulation. For both Si and Ge, the last 100 time steps of the simulation were incorporated into a histogram giving the average radial distribution. For distances greater than the length of the supercell, no new information is collected in calculating the radial distribution function of the liquid. At half the distance, it is possible for the particles to begin to sense the supercell geometry. It is possible to make use of some information in the radial distribution function for distances greater than half the cell size, but this procedure is complex and yields poor statistics.

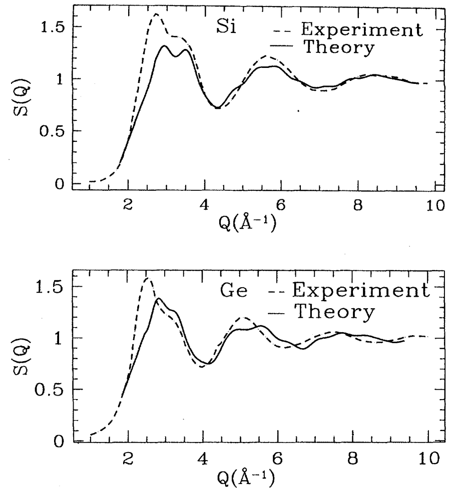

FIG. 2. Theoretical (solid line) and experimental (dashed line) structure functions, $S(Q)$, for Si and Ge.

In Fig. 1, we compare our calculated results with the pair-correlation functions taken from neutron measurements.[26] For silicon, there is a good agreement for first peak: 2.40 Å from experiment and 2.43 Å from theory. For germanium, the agreement is not as good. We find a 4% difference in the first peak positions for Ge. One problem with the current simulation is that we have fixed the density of the liquid. It may be that the theoretical density at this temperature is not entirely consistent with experiment. For example, the calculated lattice constant for crystalline germanium is too small compared to experiment by a few percent. This error which can be attributed to the local-density approximation may be also reflected in the liquid state.

The calculated structure factor function $S(Q)$ is represented in Fig. 2 along with experimental data.[26] Although we are limited by the size of our supercell in performing the transform of $g(R)$ into $S(Q)$, we obtain fairly reasonable structure factors.[16] The calculated structure factors for both Si and Ge have an asymmetric shoulder on the first peak. This feature agrees with the experimental results. The presence of this shoulder indicates that semiconductor liquids have a more complex structure than simple liquids. For example, this shoulder is absent in liquid tin and liquid lead.[3] The shoulder is more pronounced in Si as opposed to Ge. This is consistent with the more metallic behavior of Ge when compared to Si. Also, the rapid damping of $g(R)$ shows that the packing of atoms in liquid Si and Ge cannot be replicated by hard-sphere packing as can be done for simple liquid metals. The origin of this shoulder is related to the depth of the first minimum of $g(R)$ which follows the first peak. For a more structured liquid, the depth of this minimum is accentuated. The position of the first peak in the structure factor has an 8% discrepancy with experimental data for Si and a 10% discrepancy for Ge. The first peak for Ge is shifted to the right more so than the corresponding peak in Si. This is expected because of the difference in $g(R)$ for Si and Ge. For other peaks, the discrepancy for the second peak is 5% for Si and 10% for Ge, for the third peak: 3% for Si and 5% for Ge.

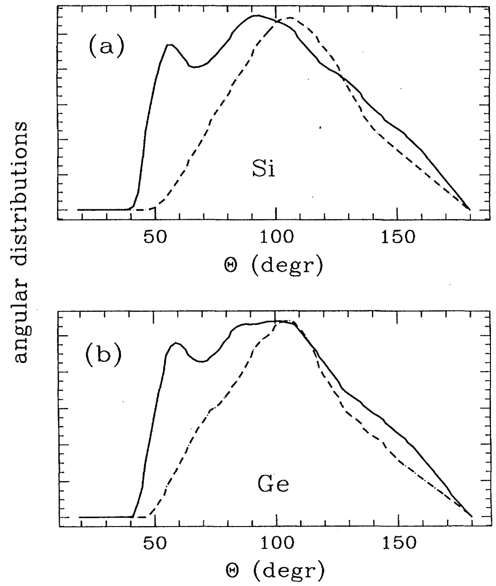

FIG. 3. Angular correlation functions, $g(\theta,R_m)$ (solid line) and $g(\theta)$ (dashed line), for Si (a) and Ge (b). See text for definitions of $g(\theta,R_m)$ and $g(\theta)$.

Some of these discrepancies may arise because of technical differences in the transformation from $g(R)\rightarrow S(Q)$ in theory and $S(Q)\rightarrow g(R)$ in experiment. For example, artifacts from the supercell can exist in the theory and $Q$ cutoffs in the experiment can affect the transformation to $g(R)$. It is also possible that $g(R)$ will start to reflect periodic boundary conditions when $R$ exceeds half the cell size. However, this does not appear to be a serious limitation on defining the salient features of the distribution function.[16] With respect to the integration procedure in transforming $g(R)\rightarrow S(Q)$, we integrate out to $R=L$ where $L$ is the edge size of the cell.

Given the nature of the many-body interactions in silicon, or germanium, it is interesting to examine the angular distribution function, or pair-correlation function of order higher than 2. In Fig. 3, we show the angular functions for both Si and Ge. We plot unnormalized angular functions so that a homogeneous distribution of atoms would be a $\sin(\theta)$ curve. We distinguish two types of angular distribution functions. The first type of angular distribution function, $g(\theta)$, considers an angle defined by a vector drawn from a reference atom to the nearest atom, and a vector drawn from the reference atom to the next-nearest atom. The second type of angular distribution, $g(\theta,R_m)$, is an average of angles between a reference atom to the nearest atom, and a vector drawn from the reference atom and all pairs of atoms within a radius $R_m$ of the reference atom. In the calculations presented, as is common practice, we defined $R_m$ to be the first minimum in the pair-correlation function, i.e., 3.15 Å for Si and 3.20 Å for Ge. For both angular functions, angles below ~40° are not found. Such small angles are forbidden by steric constraints for the $g(\theta)$ distribution. In principle, such small angles could occur in the $g(\theta,R_m)$ distribution, but this could only occur for atoms which are "onefold" coordinated. The peak in both distributions near ~110° are suggestive of a fourfold-coordinated silicon atom, i.e., a covalent configuration. We expect Si and Ge to be less covalent and become more metalliclike in the liquid state. This is reflected in the existence of a peak near ~60° in the distribution function. Such an angle would occur in a close-packed solid. In the solid state, covalent bonds in Si and Ge are shorter than metalliclike bonds. If this trend persists in the liquid state, then we would expect shorter bonds to favor a locally tetrahedral arrangement as indicated in the $g(\theta)$ distribution. If we only had a metalliclike arrangement in the angular function, then we might expect the distribution shown in the $g(\theta,R_m)$ distribution. For example, in the hexagonal close-packed structure for a metallic system, we would expect distinctive peaks at 60° and at 90°. Calculations using interatomic potentials often do not replicate a two-peak structure; the "60° peak" is often absent.[27] This suggests the interatomic potentials emphasize the "covalent" character of the liquid at the expense of the "metallic" character.

The metallic bonding component of $l$-Si or $l$-Ge is confirmed by experimental measurements. The liquid state of these semiconductors shows no energy gap. An analysis of the liquid charge density indicates electrons in the liquid state become delocalized and contribute to conductivity.[3,17,18] The experimental results, obtained from the measurements of the Hall coefficient and electrical conductivity show that the density of conduction electrons increases by $10^9-10^{11}$ compared to solid state. While the density of electronic states increases at the Fermi level in the liquid state, the electron-scattering rate also increases in the liquid. This latter effect is due to disorder in the liquid state compared to the crystalline state. The combination of these two factors results in increase of the conductivity by a factor of 20 for $l$-Si and by a factor of 11 for $l$-Ge.[1]

In Fig. 4, we present the distribution of coordination number, $C(N)$, in $l$-Si and $l$-Ge. $C(N)$ is defined as the probability of an atom to have $N$ neighbors within the limiting sphere of radius $R_m$. We compare our results to previous theoretical work.[17,18] For both Si and Ge, the agreement with previous work is quite striking. Our calculations use a different pseudopotential, different thermalizing procedures, and different dynamics to examine the liquid state. This result suggests that the simulation of the liquid is not overly sensitive to the details of the procedure. We can determine the average coordination for the liquid state by integrating the radial distribution function up to the cutoff. We find an average coordination number of 6.4 for Si and 5.6 for Ge.

## IV. THE DYNAMICAL PROPERTIES OF LIQUID SILICON AND GERMANIUM

By following the atomic positions in the liquid state as a function of time, we can calculate the self-diffusion of Si in $l$-Si and Ge in $l$-Ge. For this calculation, we set the viscosity to zero and follow the trajectories of each atom in the liquid. The diffusion constant can be determined from[6]

$$D=\lim_{t\rightarrow\infty}\frac{\langle[R(t)]^2\rangle}{6t}, \tag{2}$$

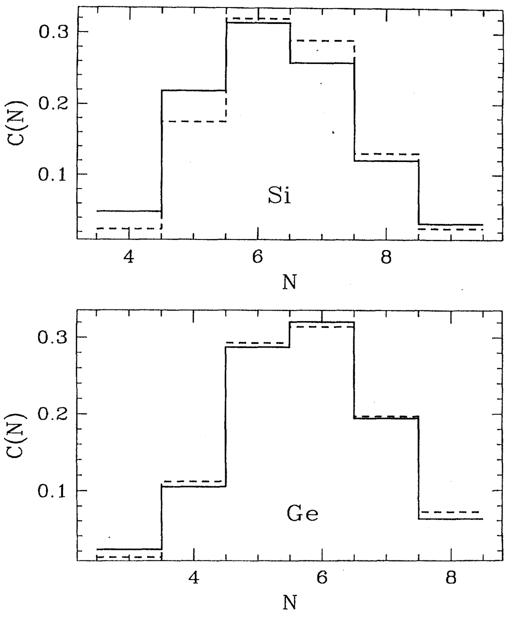

FIG. 4. Coordination number from the present calculations (solid line) for Si and Ge in comparison with theoretical results obtained in previous work (Ref. 18) for Si and for Ge (Ref. 17).

where the mean-square displacement is given by

$$\langle[R(t)]^2\rangle=\frac{1}{N}\sum_{i=1}^{N}[R_i(t)-R_i(0)]^2, \tag{3}$$

$R_i(t)$ is the position of the $i$th atom. The average is over all the atoms $N$ in the unit cell. The $t=0$ point is arbitrary, provided the simulation is performed over a sufficiently long time. One issue which merits careful attention is the center-of-mass rotation motion of the atoms in the supercell. When the simulation is initiated, the center-of-mass motion of the unit cell is taken to be zero. However, as the simulation proceeds, the Langevin thermalization procedure which contains a stochastic term does not guarantee a zero velocity for the center-of-mass motion. We have taken care to zero this motion before calculating the root-mean-square velocity.

In Fig. 5, we plot the root-mean-square displacement for both $l$-Si and $l$-Ge. In both cases, the root-mean-square displacement is quite linear with time, although some small "statistical fluctuations" are evident.

The self-diffusion coefficient for Si is approximately $1.9\times10^{-4}$ cm$^2$/sec. This value is consistent with previous *ab initio* calculations,[18] but higher than simulations based on tight-binding, or interatomic potentials. We attribute this difference to the "inflexibility" of a tight-binding basis which may effectively increase the kinetic barriers. The interatomic potentials are even less flexible in that they omit any electronic degrees of freedom. The diffusion coefficient for Ge is $1.0\times10^{-4}$ cm$^2$/sec. Again, this value is in good agreement with other *ab initio* calculations.[17] We summarize calculated values for the self-diffusion coefficient in Table I.

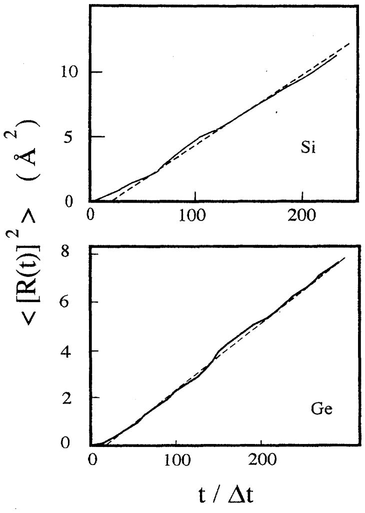

FIG. 5. The time dependence of the mean-square displacement in liquid silicon and germanium. The straight lines are fit to the simulation for $t>100\Delta t$.

## V. CONCLUSIONS

We have presented a molecular-dynamics approach using quantum forces for simulating the properties of liquid semiconductors. We focused on examining the liquid properties of Si and Ge. Our approach uses Langevin dynamics with quantum forces to thermalize the system. When the desired temperature has been achieved, we "turn off" the viscous heat bath present in the Langevin dynamics. This procedure allows us to prepare the system with the desired temperature in a "natural" manner. We have tested this procedure starting from two different initial conditions. In the case of Si, we initiated the simulation from a crystalline configuration. In the case of Ge, we initiated the simulation using a random configuration of atoms. The random configuration appears to be a more realistic starting point; however, in both cases, we obtained results consistent with previous work based on an initial crystalline environment. The lack of sensitivity of our

TABLE I. Self-diffusion constant $D$, for liquid silicon and germanium as calculated from various theoretical methods.

| Self-diffusion parameter ($10^{-4}$ cm$^2$ s$^{-1}$) | Si | Ge |
|---|---|---|
| *ab initio* simulations | | |
| Microcanonical ensemble with quantum forces | 1.9 | 1.0 |
| Car-Parrinello with Nosé | 2.1[a] | 1.0[b] |
| Semiempirical simulations | | |
| Tight binding [c] | 1.7,1.3,1.1 | |
| Empirical simulations | | |
| Interatomic potentials [d] | 1.0 | |

[a] Reference 18.
[b] Reference 17.
[c] References 4–6.
[d] Reference 7.

simulation to the initial state is very reassuring as it reinforces the validity of our assumptions with respect to the construction of a realistic liquid ensemble.

Once the system is thermally prepared, there is no need for any *ad hoc* dynamics to control the temperature. Our procedure allows the system to remain on the Born-Oppenheimer surface. Energy states are occupied in straightforward fashion for metallic systems. We take much longer time steps than in the Car-Parrinello approach. These longer time steps compensate for the additional computational labor of obtaining a self-consistent solution for each time step.

In our simulations, we are able to predict structural properties of liquid semiconductors such as the pair-correlation function, angular correlation functions, the structure factor, the distribution of coordination number, and the self-diffusion coefficient. Our calculated pair-correlation functions and structure factors are in good agreement with experimental data. We also considered two types of angular distribution functions. The first type of angular distribution function, $g(\theta)$, considers an angle defined by a vector drawn from a reference atom to the *nearest* atom and a vector drawn from the reference atom to the *next-nearest* atom. The second type of angular distribution, $g(\theta,R_m)$, is an average of angles between a reference atom and *all* pairs of atoms within a radius $R_m$ of the reference atom. If we considered only nearest neighbors to determine an angular distribution function, we observe a predominantly "covalent" bonding configuration, i.e., the distribution is strongly localized around the tetrahedral angle. If more distant neighbors are considered, then a more "metallic" configuration is observed, i.e., there is a peak in the function near angles appropriate to close-packed structures. This situation is consistent with both covalent and metallic bonds coexisting in the liquid state.

## ACKNOWLEDGMENTS

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