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STRUCTURE AND PROPERTIES OF SIMPLE MOLECULAR SYSTEMS AT VERY HIGH DENSITY

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The use of computer simulations in the study of molecular systems at very high density is reviewed. Applications to the thermodynamics of dense fluid nitrogen and phase transitions in solid oxygen are presented. The effects of changes in the atomic electronic structure on the equation of state of very dense helium are discussed.

KEY WORDS: Computer simulations, Electronic structure, Helium

INTRODUCTION

Traditionally, theoretical studies of condensed molecular systems have concentrated on either physical or electronic properties, with relatively little effort in the coupling of the two. We describe here some of the tools available for studying phase transitions and thermodynamics, i.e. physical properties, but also show that changes in the electronic structure cannot be ignored at extremely high density.

The most useful techniques in the theoretical study of the physical properties of condensed molecular systems are molecular dynamics (MD) and Monte Carlo (MC) computer simulations. These methods can be used not only for the calculation of bulk structure and thermodynamic quantities, but also for details of molecular order and correlations not available experimentally. Many reviews and pedagogical articles are available on the use of these techniques (Ciccotti and Hoover, 1986; Ciccotti *et al.*, 1987; Frenkel, 1989).

For bulk systems, computer simulations are performed by placing a relatively small number of particles ($10^2 - 10^3$) in a transparent box and then replicating that box to fill space (periodic boundary conditions). In a fluid, the choice of box shape is relatively unimportant; there is no long range symmetry. In a solid, however, some crystal structures may be representable by a certain box shape, while other structures may not. Parrinello and Rahman (1980) introduced a method for MD simulations at constant stress that enabled the box to change shape in the simulation, thus allowing for phase transitions accompanied by changes in crystal symmetry. Use of a box with variable shape is also straightforward for molecular systems (Nosé and Klein, 1983) and in MC calculations (Frenkel, 1989).

The input to a computer simulation are the descriptions of the interactions between the molecules. In most computer simulations, the interaction energy is approximated as a sum of pair potentials, ignoring many-body effects. The many-body interactions include dispersion (van der Waals) forces and the many-body short-range interactions due to the overlap of more than two charge distributions. In the rare-gas solids, these interactions can be important, even at relatively low density (Barker, 1989). At very high density, changes in the electronic structure of the constituents become important many-body contributions (LeSar, 1983; LeSar, 1988).

For molecular systems, a representation of the potential is needed that can describe the orientational dependence. In most computer studies, the potential is written as a sum of distance(only)-dependent interactions between sites in the molecules (site-site potentials). Price (1987) has recently examined this approximation for diatomic molecules. The parameters that define the potential can be determined by either fitting to gas phase data and/or theoretical calculations of the pair potential or by fitting calculated results to solid state data.

The latter approach builds into the potential some estimate of the many-body terms and thus may be better for condensed-phase applications.

STRUCTURE AND THERMODYNAMICS

Using a site-site potential for nitrogen determined by fitting to experimental and theoretical results, Belak *et al.* (1988) performed MC simulations to calculate the volume and enthalpy in dense fluid N_2 at pressures up to 30 GPa and temperatures up to 3000 K. By fitting the calculated volumes and enthalpies to analytical expressions, a set of thermodynamic quantities (heat capacity, adiabatic compressibility, etc.) were derived. The calculated values show good agreement with experiment (Mills *et al.*, 1975) up to 2 GPa near room temperature for the volume (within 0.3%) and the speed of sound (within 1%). Since this potential also yields good agreement with the room-temperature equation of state to 10 GPa, it should provide reasonably reliable thermodynamic "data" over a wide range of pressures and temperatures. One quantity of interest is Grüneisen parameter (γ_θ). Our results indicate that an assumption which is often used in analyzing shock data, namely that $\rho\gamma_\theta$ is constant along the Hugoniot, is not very accurate. This result agrees with other recent studies (Shaner, 1988).

Solid oxygen is an excellent example of how constant-pressure Monte Carlo methods with variable-box shape can be used to study solid-solid phase transitions. Since many of the crystal structures in oxygen are related to each other by simple shears, transformations are easy. We modelled the intermolecular potential by a site-site potential fit to experimental gas phase and solid state data and used a classical Heisenberg model to describe the magnetic interactions (LeSar and Etters, 1988). We calculated the zero pressure, low temperature, α (antiferromagnetically ordered) $\rightarrow \beta$ (magnetically disordered) transition and found excellent agreement with experiment. The calculated magnetic

Figure 1: Pressure vs volume for solid helium at room temperature: experimental results (Mao *et al.*, 1988) [closed circles], calculations with the gas-phase potentials of Aziz *et al.* (1987) [open circles] and Ceperley and Partridge (1986) [X's], a gas-phase electron-gas potential [dashed curve], the Ross-Young (1986) effective potential [bursts], and the present calculations that incorporate changes in the electronic structure [solid curve].

structure is also in good agreement with that inferred from experiment.

ELECTRONIC STRUCTURE AT HIGH DENSITY

In Figure 1 we compare the volume-pressure curve for helium at room temperature measured by Mao *et al.* (1988) with calculations based on gas-phase pair potentials. Since the gas-phase pair potential is accurately known (Aziz *et al.*, 1986), we can ascribe differences between the experiment and the calculations to many-body forces. The disagreement between the gas phase potential calculations and experiment is very large, with an error in pressure of over 30% (about 6.8 GPa) and in volume of over 3% at the smallest volume studied. We analyzed the contributions from various many body interactions (LeSar,

1988) and found that the many-body dispersion terms contribute only about 0.1 GPa and the many-body short-range energy only about 0.2 GPa to the pressure at the highest density studied, which is not enough to account for the large deviation from experiment.

We also determined the change in the ground-state electronic structure of helium using a perturbation scheme based on local-density-functional theory (LeSar, 1988). The output of these calculations was, for each volume, the helium wave function, from which the (volume-dependent) intermolecular potentials were determined. These potentials were then used to calculate the equation of state. In Figure 1 we show the results of these calculations. While the agreement is still not perfect (the present results are 9% high in pressure and 3% in volume) it is evident that inclusion of the electronic structure changes greatly improves agreement with experiment. We note that this is a many-body effect that depends on the crystal structure.

In Figure 2 we show how the electronic structure of the helium atoms changes with volume. We plot $\langle r^2 \rangle / \langle r^2 \rangle_g$, the ratio of the mean-square radius of the atomic wavefunction to that in the gas phase. As the volume decreases, the atomic wave functions are compressed. Also shown in Figure 2 are the experimental values determined recently by LeToullec *et al.* (1989). At small volumes, the calculated compression of the atoms is underestimated ($\langle r^2 \rangle / \langle r^2 \rangle_g$ is too large), which could account for the remaining disagreement with the experimental equation of state.

Ross and Young (1986) developed an effective potential for helium by fitting to shock Hugoniot data. Results with their potential are shown in Figure 1 and agree with experiment about as well as the present results. Thus, one could use their effective potential in a computer simulation and hope to include at least an approximate treatment of the dominant many-body terms. This

Figure 2: Ratio of the mean-square radius of the crystal-atomic wave function to the gas-phase value ($\langle r^2 \rangle_c / \langle r^2 \rangle_g$) for solid helium. The circles are the calculated results (LeSar, 1988) and the triangles the experimental results (LeToullec *et al.*, 1989).

procedure was used in a recent path-integral Monte Carlo study of melting in helium at high density (Barrat *et al.*, 1989)

CONCLUSIONS

From the calculations on nitrogen and oxygen, it is clear that using realistic descriptions of intermolecular potentials in computer simulations can yield accurate results for the bulk structural and thermodynamic properties of condensed molecular systems. The work on helium, however, strikes a note of caution. As the density is increased, the effects of the local environment on the electronic structure of the constituent molecules and thus the interaction potentials can become considerable. These changes make application of potentials found in one density region suspect when applied to a region of considerably

different density.

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