Equation of State of Dense Helium

R. LeSar
Los Alamos National Laboratory, Los Alamos, New Mexico 87545

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Comparison between pressure-volume relations in helium at high pressures indicates that theoretical calculations based on gas-phase pair potentials are not adequate to explain recent x-ray experiments. Regardless of what potential is used, the gas-phase potentials give an equation of state that is much too stiff. It is shown that if the changes in the atomic wave functions induced by the high-pressure crystal environment are taken into account, then agreement between experimental and theoretical pressure-volume curves is greatly improved.

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Recent advances in diamond-anvil cell technology coupled with the use of high-intensity x-ray sources have enabled the accurate determination of the equations of state of a number of simple molecular systems at very high densities. Theoretical calculations based on gas-phase pair-interaction potentials cannot, however, account for these very-high-pressure pressure-volume data, with the calculated curves being too stiff.[1] The recent x-ray work on solid helium at room temperature in the range of 15.5 to 23.5 GPa is a good example.[2] In Fig. 1 we show the experimental pressure-volume data as well as the results from a variety of calculations. The pressure-volume curves calculated with gas-phase pair potentials are not at all close to the experimental one; indeed, the best theoretical pressures from pair-potential calculations are high by about (25–30)% in the range of volumes studied. The purpose of the present paper is to show that the softening of the experimental pressure-volume curve relative to that calculated from gas-phase potentials can be largely accounted for by a compression of the electronic structure of the constituent atoms.

Since the gas-phase pair potentials fail to describe the equation of state of helium (and other systems), one has to invoke many-body interactions to explain this discrepancy. There are a number of types of many-body interactions to consider, the most familiar of which are the many-body dispersion interactions, most often described by the first-order Axilrod-Teller term[6] which is valid at large separations. At the densities of the experiments on helium (fivefold to sixfold compressed), however, these interactions are not very important[1] and the expressions themselves are not valid for the very close nearest neighbors. Recently, a number of authors have invoked the use of "three-body exchange" terms to approximate the many-body short-range interactions.[7] While these may be important in some regimes, they do not reflect the symmetry of the local environment of the crystal and cannot be a good approximation to the many-body short-range interactions at very high densities. Indeed, results of calculations on solid argon at very high densities suggest that these terms overestimate the many-body interactions.[1] Band-structure methods determine the electronic structure of the system and reflect the symmetry of the crystal, thus including many-body interactions.[8] These are total-energy techniques, however, and cannot be used to directly determine the various contributions to the many-body effects. The method outlined in this paper allows such analysis.

A few years ago we introduced a simple theoretical technique for calculating the change in the electronic

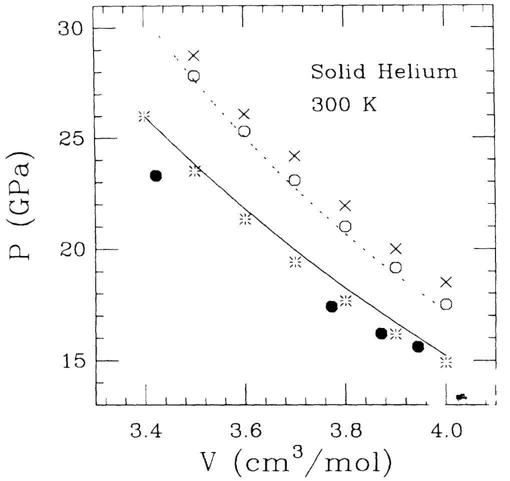

FIG. 1. Pressure vs volume for solid helium at room temperature. The closed circles are the experimental values (Ref. 2), the dashed curve is from the present theoretical calculation with a gas-phase pair-potential according to the modified Gordon-Kim model with damping function, the other symbols are the results of calculations with pair potentials (Ref. 2): The circles were calculated with the most recent gas-phase potential of Aziz, McCourt, and Wong determined from fitting to experimental data (Ref. 3); the crosses were with the gas-phase potential of Ceperley and Partridge found with quantum Monte Carlo methods (Ref. 4); and the asterisks were with the effective two-body potential of Ross and Young extracted from shock-Hugoniot data (Ref. 5). The solid curve is from the present study and incorporates the changes in the crystal-atomic wave functions.

structure of closed-shell atoms and molecules in a crystal.[9] This approach, which we called the crystal-perturbation model (CPM), was applied to Ar and Xe, where we examined changes in the ground- and excited-state atomic wave functions. We found that at high densities the atomic wave functions were compressed, i.e., their radial extent decreased. This atomic compression led to a modest softening of the pressure-volume curves. Recently, Barker found that by adding this volume correction to the results of calculations based on an accurate *ab initio* gas-phase pair potential, the agreement between the theoretical and experimental pressure-volume curves in high-density argon was greatly improved.[1]

The principal assumptions behind the CPM are (1) the electrons in a molecular crystal are tightly bound to their molecular sites; (2) the effects of the crystal environment on the electronic ground and excited states can be treated as a perturbation on the free-atomic states. One considers the Hamiltonian for a chosen atom m in a crystal as a sum of the usual gas-phase atomic Hamiltonian H_a and a crystal-potential term $V(\mathbf{r})$, i.e., $H_m = H_a + V(\mathbf{r})$. The crystal potential is defined as $V(\mathbf{r}) = V_{\mathrm{TFD}}[\rho_T] - V_{\mathrm{TFD}}[\rho_m]$, where the Thomas-Fermi-Dirac crystal potential, V_{TFD}, is given by the functional derivative of the energy of a noninteracting electron gas,

$$E[\rho] = \int d^3r \{C_k \rho^{5/3} - C_x \rho^{4/3} + E_c[\rho] + \rho\Phi[\rho]\}, \quad (1)$$

which yields

$$V_{\mathrm{TFD}}[\rho] = \tfrac{5}{3} C_k \rho^{2/3} - \tfrac{4}{3} C_x \rho^{1/3} + E_c'[\rho] + \Phi[\rho].$$

The terms in V_{TFD} represent the kinetic, exchange, correlation, and Coulomb potentials, respectively. The constants C_k and C_x are the usual constants for the noninteracting-electron-gas kinetic and exchange density functionals.[10] To correct for problems such as the exchange self-energy, these constants are then multiplied by numerical factors that depend only on the number of electrons.[11] In our applications, we used the correlational-energy functional, E_c, of Gordon and Kim.[10,11] ρ_T in $V(\mathbf{r})$ is the total electronic density of the system and is the sum of the electronic densities of all the atoms in the system. ρ_m is the electronic density of the chosen atom. The perturbation term is added to the atomic Hamiltonian and the wave function and energy determined with standard Hartree-Fock techniques.[9]

Although the experiments showed that helium has an hcp structure in this region of pressure, we approximated that structure with an fcc lattice in the determination of the crystal-atomic wave functions. Since the nearest neighbors are the same in the two structures, this is a reasonable approximation. By expanding the crystal potential in the Kubic harmonics,[12] we find that only the spherically symmetric first term couples to the s states of helium. Thus, the perturbation integrals in the Hartree-Fock calculations depend only on r and the atoms remain spherical. For a given volume, we calculate the crystal potential by evaluating V_{TFD} with the He gas-phase electronic density, determined with a Hartree-Fock calculation. After calculating the spherically symmetric term in the Kubic-harmonic expansion, a new He wave function is found with a Hartree-Fock calculation that includes that potential. From this wave function a new crystal potential is found. The procedure is applied iteratively, giving the crystal-atomic wave function for that volume. The change in the atomic self-energy, E_a, is determined by subtracting the Hartree-Fock energy of the isolated atom from the Hartree-Fock energy of the perturbed atomic wave function in the absence of the perturbation.

Figure 2 shows the ratio $(\langle r^2\rangle/\langle r^2\rangle_g)$ of the mean square radius of the crystal-atomic wave function to that of a gas-phase helium atom, determined from a Hartree-Fock calculation, as a function of volume for solid helium. The size of the helium atoms in the crystal decreases considerably with decreasing volume. As the size of the atoms decreases, the atomic self-energy increases because of the greater interelectronic repulsions. The increase in atomic self-energy (E_a) with decreasing volume yields a contribution to the pressure (P_a), which can be determined by finding $P_a = -\partial E_a/\partial V$. This is a very large, positive contribution, ranging from about 1.5 GPa at 4.0 cm^3/mol to 4.2 GPa at 3.4 cm^3/mol.

The energy expression in Eq. (1) is the basis for a method for calculating the interaction between closed-shell atoms and molecules, the modified Gordon-Kim electron-gas model (MGK).[10] The only inputs are the electronic densities of the interacting atoms, for instance, the isolated-He-atom densities to calculate the gas-phase pair potential. Application to uncharged species requires the addition of the long-range dispersion terms, which modify at short range with a damping function (the MGKD model).[13] The MGKD model can be used to

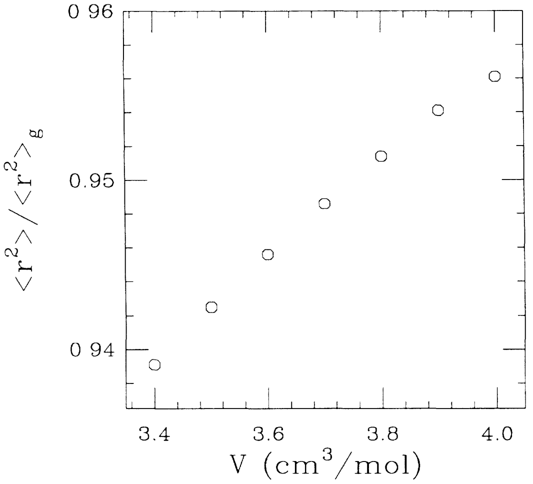

FIG. 2. Ratio of the mean square radius of the crystal-atomic wave function ($\langle r^2\rangle$) to the gas-phase value ($\langle r^2\rangle_g$) as a function of volume for solid helium. The gas-phase value is 2.369 (bohrs)^2.

evaluate the 0-K lattice energy in two ways, either by finding the pair-interaction potentials and performing a simple lattice sum, or by determining the lattice energy of the whole unit cell directly,[14] without reference to pair potentials. This latter approach includes the short-range energy due to the mutual overlap of more than two atoms, which here we shall call the many-body short-range energy.

The output of the CPM calculations consists of the atomic wave functions as a function of volume. These crystal-atomic wave functions can be then used with the MGKD model to determine the 0-K lattice energies. From the lattice energy versus volume, we can determine the lattice-energy contribution to the pressure (P_l) by taking the derivative with respect to volume as before. Note that the coefficients in the dispersion energy, which depend on the polarizabilities of the helium atoms, must change as the helium-atom electronic structure changes.[9,15] We assumed an hcp structure in the lattice calculations.

To compare with the experimental data, we need to include the thermal contributions to the pressure, P_T. For the gas-phase pair potential, constant-volume, 300-K, Monte Carlo calculations were performed and P_T determined from the change in the average of the virial. The situation is a bit more complicated with the volume-dependent CPM interatomic potentials, since the virial for use with volume-dependent potentials includes a term that is the derivative of the potential with respect to volume.[16] We do not have a convenient way to parametrize the volume dependence of the potential, and so we assumed that that term was temperature independent and found the thermal contribution to the pressure as we did for the gas-phase potentials, using a pairwise approximation for the volume-dependent potential. The thermal pressure is roughly linear in volume in this region and contributes about 2 GPa to the total pressure.

For a given volume, the net pressure is given as a sum of the different contributions, $P = P_l + P_a + P_T$. The magnitudes of these contributions at 3.4 cm^3/mol, for example, are 19.4, 4.2, and 2.4 GPa, respectively. At the same volume, a gas-phase potential gives a P_l of about 29.3 GPa. The positive contribution to the pressure from the atomic self-energy P_a is greatly outweighed by the decrease in the lattice pressure P_l due to the compression of the atoms.

In Fig. 1 we plot the room-temperature pressure-volume results of the present calculations, both with a gas-phase MGKD potential and with the volume-dependent CPM potentials. We note that the results with the MGKD gas-phase pair potential are in very good agreement with those based on the newest potential from Aziz, McCourt, and Wong[3] but are in serious disagreement with experiment. Comparing the CPM results with the experimental values, however, indicates that a large part of the discrepancy is removed when the atomic compression is included. While at 3.4 cm^3/mol the present results are still high in pressure by about 9%, the error in the pair-potential calculations is over 3 times as great. The present results compare very well to calculations based on the effective potential of Ross and Young,[5] which was determined by fitting to the Hugoniot data and thus includes an approximate description of the many-body interactions.

There are many contributions to the lattice energy that can be considered as "many-body" interactions. We calculated the CPM lattice energy with a method that gave the many-body short-range contribution to the energy due to the overlap of more than two atoms. We also calculated pair potentials for each volume with the CPM wave functions and evaluated the lattice energies with these. From these results, the many-body short-range contribution to the pressure could be found. This term is small, on the order of about 0.2 GPa in this volume range. We also included in our lattice energies the many-body dispersion terms using the lattice sums and approximations of Doran and Zucker[17] based on the coefficients for helium of Tang, Norbeck, and Certain.[18] We damped these with the same damping function (at the nearest-neighbor distance) as used for the pairwise dispersion energy. These terms were not important (less than 0.1 GPa). Indeed, the pairwise dispersion contributions to the pressure were only about 5% of the repulsive contributions. A paper comparing many-body interactions in rare-gas solids is in preparation.[15]

The inclusion of the many-body compression of the helium atoms accounts for a large part of the discrepancy between theory and experiment. The magnitude of this effect in helium is much larger than what was seen in argon at higher pressures (80 GPa).[9,15] This is not surprising since argon in that range has been compressed by about 3 times relative to its zero-pressure density. In the range of pressures of the helium experiments, however, helium is up to sixfold compressed. By corresponding-states arguments, helium at 20 GPa is at a much higher relative pressure than argon at 80 GPa.

It is difficult to assess the possible errors in the calculated pressure. The error associated with the determination of the derivative of the energy with respect to volume is small, on the order of 0.1 GPa or so at most. Thus, the errors are more subtle, and depend on the model itself. There are a number of sources of error in the model. First of all, the MGKD model yields only approximate potentials. Our experience, however, is that gas-phase pair potentials determined with this model are in good agreement with other potentials for the same system. This is born out in Fig. 1, where the pressure-volume curve calculated with the gas-phase MGKD model agrees very well with that calculated with the most recent Aziz potential. There is less direct evidence about the quality of the crystal-perturbation model. The recent work of Barker,[1] which involves adding the CPM correction to a pressure-volume curve for Ar calculated with an accurate theoretical potential, seems to indicate that the CPM volume change associated with the compression of the Ar atoms can account for the discrepancy between experiment and theory. However, the volume changes are small (about 3% at 80 GPa) and there is only one case with which to compare. That the use of the CPM accounts for a large part of the difference between theory based on pair potentials and experiment in He is encouraging, but only suggests that the current model may be correct. Preliminary Monte Carlo simulations on He with gas-phase pair potentials and with pair potentials based on the CPM wave functions indicate that both kinds of potentials predict an fcc (or hcp) structure at very high densities; thus those properties do not provide a good test. We argue, however, that the model is physically sound and, in the absence of any other approach, should be considered. If so, then the present results indicate that the dominant many-body effect in highly condensed rare-gas and molecular systems is likely to be the change in the electronic structure of the constituent molecules, not unlike the situation in ionic crystals, where the large electrostatic forces greatly perturb ionic and molecular charge distributions.[14]

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