Three-Body Exchange Interaction in Dense Helium

P. Loubeyre
Physique des Milieux Condenses, Université Pierre et Marie Curie, 75230 Paris Cedex 05, France
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Self-consistent phonon and Monte Carlo calculations show that the three-body exchange interaction is important in dense helium. Together with a realistic pair potential and the Axilrod-Teller three-body dispersion interaction, it brings calculations into agreement with the experimental equation of state. This interaction stabilizes the hcp structure for pressures greater than about 60 GPa. A speculative phase diagram of high-pressure helium is proposed.

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Studies on helium have played an outstanding role in increasing our basic understanding of matter. Two well-known examples are the studies on liquid helium, which helped to work out quantum statistical theories,[1] and measurements on its low-pressure solid phases, which were used to test highly anharmonic theories of solids like the self-consistent phonon approach.[2] Now, diamond-anvil-cell and shock-wave experiments on helium probe the evolution of highly compressed insulators, and the recent discovery of a triple point on its melting line[3] around 300 K has initiated several theoretical papers[4-7] and led to a comparison among various descriptions of dense liquid[8] and solid[9] insulators. All previous analyses rely on a major assumption, which is that the interactions of the system are well described by a pair potential; among the elements this should be best satisfied for helium. It is thus of crucial importance to test the validity of such a hypothesis. Furthermore, there is renewed interest in the contribution of three-body interactions to the analysis of measurements on dense rare-gas solids and fluids. On this point two types of calculations have been put forward: The first tends to confirm, as has been known for many years in the lower-density region, that an adequate pair potential together with the Axilrod-Teller three-body interaction leads to accurate descriptions of dense rare gases, even under pressures up to 100 GPa[10-12]; other authors claim that the three-body exchange interaction must be taken into account.[13-15] In this context a recent analysis of the equation of state of dense fluid helium and its solid-fluid equilibrium curve around room temperature has shown that the best agreement was obtained with a pair potential that is somewhat softer than the best "experimental" one[3]; this discrepancy stresses the importance of the three-body exchange interaction dense helium, with its negative contribution softening the apparent pair potential.[16] A similar conclusion was obtained for dense argon.[14,15]

The aim of this paper is to show that adding the contribution of the three-body exchange interaction to the pair-potential calculation brings it into perfect agreement with experiment. In contrast with the effective-potential approach,[14,16] it leads to a prediction of an fcc-hcp structural solid phase transition around 60 GPa and 300 K. To the author's knowledge it is the first time that such a quantitative approach has been made, apart probably from the pioneer work of Ree and Bender on dense H_2.[17] Helium is the best candidate since the pair potential and three-body interactions are known with reasonable accuracy, because of the simplicity of the electronic structure of helium atom; also the conclusions on the magnitude of the three-body exchange interaction can be extended *a fortiori* to heavier rare gases since they have larger many-body interactions.

In the study of many-body forces it is important to use the best available pair potential, since otherwise the conclusions would of necessity be biased. In the following the Aziz pair potential[18] will be used; it was fitted to the second virial coefficients, He_2 dimer energy levels, thermal-conductivity, high-temperature viscosity, and differential cross-section measurements. It adequately reproduced a sizable number of experimental data which test the pair potential at various interatomic distances. As recently proposed, it is complemented at small interatomic distances ($r < 1.828$ Å) by the Cepperley-Partridge (CP) form[19]; but in the present investigation of the fcc-hcp phase transition that will only matter above 60 GPa.

The first set of data analyzed here are the measurements of the equation of state of helium along the 4.2-K isotherm between 0.2 and 2 GPa by Stewart.[20] In Fig. 1 they are compared to the pair-potential calculation. The theoretical method used, noted SCH+CE, is the self-consistent harmonic calculation corrected for the cubic anharmonic term calculated in an Einstein approximation with a corrective multiplicative constant which was adjusted to Monte Carlo free-energy calculations. Since I have previously used the same description and program for the analysis of the fcc-bcc phase transition in helium around its 300-K triple point[5] and of the properties of solid argon,[15] the essential equations and details of implementation can be found in those two papers. Recently I have used it under the extremely anharmonic conditions of the hcp-fcc phase transition in low-density heli-

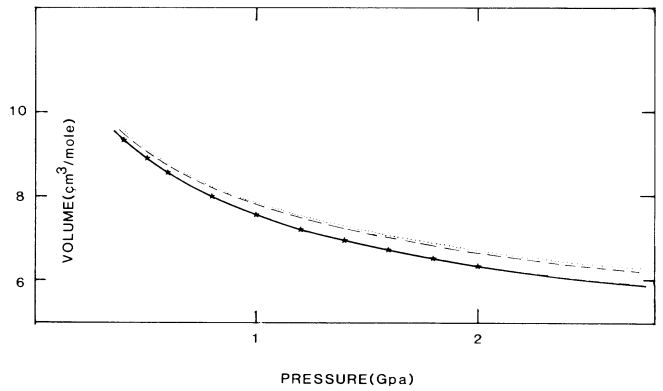

FIG. 1. Comparison between different 4.2-K equations of state of solid ^{4}He: stars, experimental measurements of Stewart (Ref. 20); dashed line, SCH+CE model with Aziz pair-potential interaction; dotted line, AT interaction is added to the SCH+CE model; full line, exchange (EXC) and AT three-body interactions are added to the SCH+CE description.

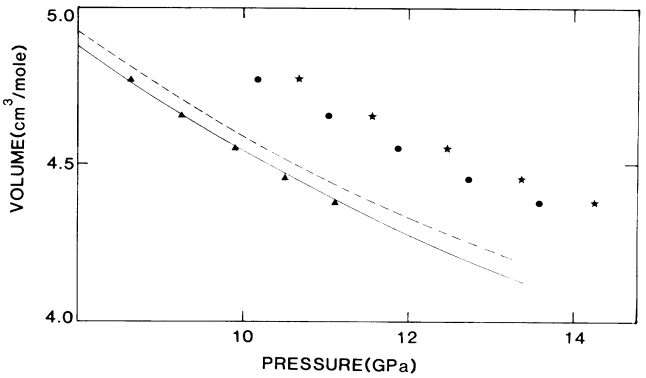

FIG. 2. Comparison between different 300-K equations of state of liquid ^{4}He: dots, Monte Carlo results; stars, quantum corrections (Q) are added to the Monte Carlo results; triangles, three-body interactions (3B) and quantum corrections are added to the Monte Carlo results; full line, Brillouin-scattering measurements (Ref. 26); dashed line, extrapolation of Mills's measurements (Ref. 27).

um[21] and it has been shown to be reasonably accurate for volumes smaller than 7.5 cm^3/mole at $T=6$ K where the anharmonic effects are not too large. The volumes calculated with the Aziz pair potential are systematically above the experimental equation of state; this once more illustrates the fact that the Aziz pair potential is too stiff to agree with experiment. This is also evidence that three-body exchange interaction, with its negative contribution that softens the pair potential, is important in helium at these densities, as noted before.[15,16]

Brunch and McGee[22] have proposed a Slater-Kirkwood–type nonadditive three-body energy in helium, V_3, that will enable us to do a more quantitative analysis:

$$V_3=\{-A\exp[-a(r+s+t)]+C(rst)^{-3}\}\times(1+3\cos t_1\cos t_2\cos t_3), \quad (1)$$

where r,s,t are the sides and t_1,t_2,t_3 the interior angles of the triangle formed by the three atoms. The first exponential term of this equation represents the exchange three-body interaction which at small interatomic distances describes the alterations of the charge densities of two interacting molecules by the presence of a third one. The constants $A=1.336\times10^{-9}$ erg and $a=1.936$ Å^{-1} were adjusted to the calculations of Novaro and Bertran-Lopez,[23] the accuracy of which was recently confirmed by Jeziorski, Bulski, and Piela.[24] The second term, known as the Axilrod-Teller (AT) one, is the exact form of the triple-dipole interaction which is the dominant contribution of the three-body interaction in the dispersion region; it is obtained by third-order Rayleigh-Schrödinger pertubation theory, and $C=2.1005\times10^{-13}$ erg Å.[9]

The three-body contribution to the SCH+CE free energy is calculated by summing the AT term over all distinct triplets of the fcc lattice. The three-body exchange interaction, which only affects the immediate neighborhood of an atom, is calculated by summing over all the different triplets formed by two nearest neighbors surrounding a central atom (66 for the fcc or hcp structure), with a multiplicative constant of $\frac{1}{3}$ for equilateral triangles to prevent double counting. Rigorously, this is only the contribution to the static lattice energy, but the dynamical one, being much smaller, is neglected here. The equation of state is then calculated by volume differentiation of the free energy. In Fig. 1, we see that adding only the AT contribution slightly increases disagreement with experiment; but if the exchange three-body interaction is then added, the agreement with experiment becomes excellent. This definitely points to the exchange three-body interaction as being important in dense helium. It would then be most interesting to extend such an analysis to higher densities. Diamond-anvil-cell techniques (DAC) are required to achieve higher pressure, but doing x-ray experiments in a DAC to measure the helium equation of state as was done for heavier rare gases[14,25] seems to present too great an experimental difficulty at the present time. Nonetheless, Polian and Grimsditch, using a DAC Brillouin-scattering technique, have recently measured the velocity of sound in liquid helium at room temperature up to 12 GPa.[26] These data were integrated to evaluate the liquid equation of state up to the freezing point. It probes the helium interaction at higher densities than in Stewart's case but the uncertainty on the volume is larger than 5%.

In Fig. 2 I compare these experimental data with the liquid equation of state calculated by Monte Carlo simulation on 432 helium atoms interacting with the Aziz pair potential.[6] As from Fig. 1 I conclude that the discrepancy with experiment is caused by the stiffness of

the Aziz potential. But for a more complete comparison two contributions have to be added: the three-body interactions as shown above, but also the quantum corrections which are known not to be entirely negligible at these densities. For computational simplicity I have estimated both corrections on an fcc structure, but the error introduced in this way should be quite small since the fcc solid and liquid pair distribution functions are very similar near the melting line, at least up to the second neighbors.[6] The quantum correction to the free energy is estimated by the h^2 term of the Wigner-Kirkwood expansion. The three-body contribution is estimated as explained above.

In Fig. 2, the positive quantum contribution to the pressure increases the discrepancy between theory and experiment; this confirms that the Aziz pair potential is too stiff to describe the system. The large negative-pressure contribution of the three-body interactions, which is the sum of the positive AT part and the dominant large negative three-body exchange one, gives a good fit with experiment, as seen in Fig. 2. This extends the previous conclusions to higher densities; i.e., three-body exchange interaction is important in dense helium, leading to a 20% negative-pressure contribution around 10 GPa. There is only a slight discrepancy with Mills's equation of state[27] which is fitted to measurements up to 2 GPa and extrapolated here up to 12 GPa, as also seen in Fig. 2.

We can now wonder what the differences are between the present approach which explicitly takes into account three-body interactions and others which would incorporate them in an effective pair potential fitted to experimental data. The main difference, which could be probed experimentally, is that the first predicts that an fcc-hcp phase transition is induced in helium at around 60 GPa at $T=300$ K by the three-body exchange interaction. We can grasp an intuitive idea of it from the following reasoning: Since, as first pointed out by Axilrod,[28] the AT interaction favors the fcc structure over the hcp one, and since the exchange interaction has the same geometrical dependence [as seen in Eq. (1)], is of opposite sign, and dominates at high densities, it consequently follows that hcp should be favored over fcc by the three-body exchange interaction at high densities. For a more quantitative prediction, I thus have calculated the free energy of each structure as explained above in the calculation of the $T=4$ K solid equation of state; a double tangent Maxwell construction then gives a pressure of 60 GPa for the fcc-hcp transition, practically independent of temperature between 4 and 300 K. This value for the transition pressure is much lower than the previous linear-muffin-tin-orbital (LMTO) one[29] based on a band-structure calculation, namely, 1100 GPa at $T=0$ K; but McMahan[30] has pointed out that this value should be considered as an upper bound since below this pressure, the free-energy difference between fcc and hcp is of the same order as the uncertainties of the LMTO calculations.

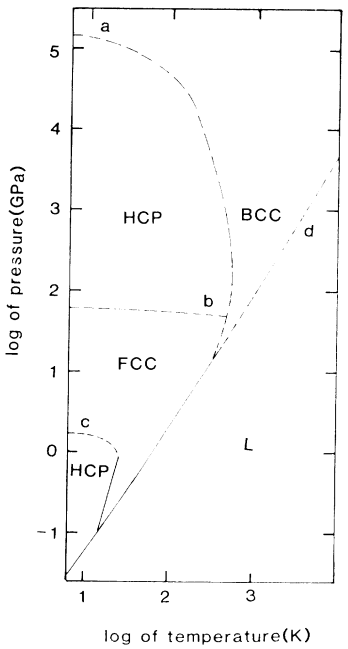

FIG. 3. Hypothetical phase diagram of ^{4}He; the pressures and temperatures are plotted on logarithmic scales. The full lines indicate experimental determinations of the low-density fcc-hcp phase transition (Ref. 31) and of the melting curve (Ref. 3). The calculations are plotted as dashed lines; in region *a*, they are the LMTO ones of Ref. 29; in region *b*, the ones of the present work; in region *c*, the ones of Ref. 32; in region *d*, the ones of Refs. 3 and 29.

At still higher pressures, the band-structure calculations predict a transition to a bcc phase. The hcp-bcc transition is also obtained by the present calculations but in a density region where the present treatment of the many-body forces is likely to be unreliable. Therefore this region of the phase diagram, shown as region *a* in Fig. 3, has been constructed by use of a band-structure estimate of the transition pressure.

The present calculation also gives an fcc-bcc transition in the region near the melting line with a triple point around 350 K; although it is in reasonable agreement with available experimental data,[3] the calculation is here less reliable than when thermal effects are smaller.

In Fig. 3 I have constructed a speculative phase diagram for ^{4}He based on the above pieces of information; they are completed in the low-density region by the calculations of Holian *et al.*,[32] confirmed by mine own,[21] which predict that the hcp-fcc transition line, measured up to 0.9 GPa,[31] should curve back on the $T=0$ K axis around 2 GPa. An interesting point is that most of the unknown transition lines are within reach of present experimental DAC techniques, and this should thus stimulate experimental investigations.

Finally, since many-body interactions are more important in heavier rare gases because of their less-bonded electronic environment, the present conclusions can be extended to them; I will show in a future detailed article that in argon, krypton, or xenon, the three-body exchange interaction with the AT term and the best available pair potential brings perfect agreement with the DAC x-rays equation of state up to nearly 100 GPa, and that it should also induce an fcc-hcp phase transition below 90 GPa in all these rare-gas solids.

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