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Interatomic potential for the condensed phases of helium atoms

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Results from diffusion Monte Carlo have been used in fits of a damping function of the triple dipole and of the intensity of the exchange three-body interactions. The equations of state obtained considering this three-body potential are in excellent agreement with experiment both at the solid and liquid phases. The calculations show that exchange nonadditivities that contribute less than 0.2% of the two-body potential energy in the solid phase are needed to describe the properties of a system of helium atoms.

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The observation of nonclassical rotational inertial in solid ^{4}He under torsional motion has demonstrated[1,2] a superfluid-like behavior of this phase. It was observed for helium confined both to an annular channel in a sample cell and in a porous media. It has prompted a renewed interest in the properties of the solid phase. Moreover, helium crystals are considered model systems that can reveal crucial information on properties of crystalline surfaces.[3] From the microscopic point of view, the description and understanding of the helium solid phase requires the knowledge of the interatomic potential.

The interaction energy of dimers of helium atoms can be calculated with great accuracy and with reliable estimates of their uncertainties. Very accurate helium-helium interatomic potentials can be obtained by combining these *ab initio* results.[4–6] By using one of them, properties of helium at low densities, such as the thermal conductivity and the viscosity, are determined with uncertainties smaller than those obtained in corresponding experiments. In many investigations of the condensed phases of helium it is possible to assume only the pairwise approximation of the interatomic potential.[7] However, it has been known[8] for a long time that higher-order terms are needed for a detailed description of these phases. The importance of the investigation of many-body effects is increasing as experiments and simulations become more sophisticated and show that these effects are essential in the determination of many physical properties. In fact, and not only for the helium atoms, these effects are important. In other systems, ranging from polymer colloid mixtures in the protein limit[9] to base-pairing stabilities in DNA[10] and liquid water,[11] their role is recognized.

The effective investigation of many-body effects in the interatomic potential usually requires an accurate knowledge of the pairwise additive contributions. Since for the systems of helium atoms they are already known at a very accurate level, which still continues to improve,[12] it appears appropriate to study[13–15] high order contributions to the interatomic potential of these systems. It is worthwhile to obtain an equation of state (EOS) for the solid phase at an accuracy level comparable to the one determined at the liquid phase. Interatomic potentials that in quantum Monte Carlo calculations[16] in the liquid phase give results in excellent agreement with experiment were not able to perform equally well in the solid phase.

In this work we have put together an interatomic potential that is able to give an excellent description of the EOS in both the solid and liquid phases. It has been constructed considering a two-body potential from the literature, a damped triple-dipole term, and an exchange potential. The dominant three-body effect we have considered is the triple-dipole long-range dispersion term proposed by Axilrod-Teller and Mutto (ATM).[17,18] It is obtained in the long-range limit and it is not valid at short-range distances. At these distances, a reasonable description of the system requires this interaction to be damped. Accordingly we have introduced the damping function F in the ATM term,

$$V_{DDD}(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3) = C_9 \frac{1 + 3\cos(\gamma_1)\cos(\gamma_2)\cos(\gamma_3)}{r_{12}^3 r_{13}^3 r_{23}^3} F(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3), \tag{1}$$

where γ_i and r_{ij} are the angles and sides of the triangle formed by the atoms, and $C_9 = 1.51 \times 10^{-6}$ K nm^9 (Ref. 19) is the nonadditive coefficient; and the function F we have chosen is a product of three[20] Tang-Toennies $f_3(r,\delta)$ damping functions,[21]

$$F(\mathbf{r}_i,\mathbf{r}_j,\mathbf{r}_k) = f_3(r_{ij},\delta) f_3(r_{ik},\delta) f_3(r_{jk},\delta), \tag{2}$$

with

$$f_3(r,\delta) = 1 - \left(\sum_{k=0}^{3} (\delta r)^k / k!\right) \exp(-\delta r), \tag{3}$$

where we have considered δ a fit parameter. Among the various alternatives of the literature[15,22,23] of how to damp the triple-dipole interaction term, the above one seems straightforward and avoids difficulties that more elaborate approaches might have in the calculation of the parameter δ for the helium trimer.[22]

The importance of the three-body exchange term has been debated for a long period of time, but now its contribution to explain properties of the systems of helium atoms has been acknowledged.[14,15,24] It is from the intermediate and short-range distances that come its most significant contributions. It occurs in the region beyond and relatively near the potential minimum where the number of trimers is larger than that of dimers and the nonadditivity is still significant. Despite the progress in treating exchange nonadditivities, results that differ by an order of magnitude are not totally understood.[14]

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As the three-body nonadditive exchange part of the interatomic potential of our calculation we use the Cohen and Murrell[15] form, living its intensity $\mathcal{A}$ as a fitting parameter (see also Ref. 25). The symmetry coordinates, $Q_1 = 1/\sqrt{3}(r_{12}+r_{13}+r_{23})$, $Q_2 = 1/\sqrt{2}(r_{13}-r_{23})$, and $Q_3 = 1/\sqrt{6}(2r_{12}-r_{13}-r_{23})$ are used to express this potential,

$$\begin{aligned} V_J = \mathcal{A}[&c_0 + c_1 Q_1 + c_2 Q_1^2 + (c_3 + c_4 Q_1 + c_5 Q_1^2)(Q_2^2 + Q_3^2) \\ &+ (c_6 + c_7 Q_1 + c_8 Q_1^2)(Q_3^3 - 3Q_3 Q_2^2) \\ &+ (c_9 + c_{10} Q_1 + c_{11} Q_1^2)(Q_2^2 + Q_3^2)^2 \\ &+ (c_{12} + c_{13} Q_1 + c_{14} Q_1^2)(Q_2^2 + Q_3^2)(Q_3^3 - 3Q_3 Q_2^2)] \\ &\times \exp(-\alpha Q_1), \end{aligned} \tag{4}$$

where the parameters α and c_i can be found in Ref. 15.

Along with the triple-dipole dispersion interaction, there are other multipolar nonadditive third-order contributions to the dispersion energy. However there is good evidence[26] that these contributions are canceled by the fourth-order triple-dipole term. For this reason they are not considered in our calculations. On the other hand, the exchange correlation effects are supposed to be of importance, since for the helium trimers the nonadditivity is probably dominated by the exchange forces.[15]

We describe the system of N helium atoms by the Hamiltonian

$$H = -\frac{\hbar^2}{2m}\sum_{i=1}^{N} \nabla_{\mathbf{r_i}}^2 + V(R), \tag{5}$$

where $V(R)$ is the interatomic potential, it is given by the sum of the three-body terms above and the two-body potential $V_2(R)$ proposed by Janzen and Aziz,[5] where retardation effects have been added to the dipole-dipole part of the potential proposed by Korona *et al.*[6,33] The set of all coordinates is denoted by $R=\{\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_\mathrm{N}\}$.

The ground-state energies of the systems of ^{4}He atoms we have considered were obtained by the diffusion Monte Carlo (DMC) method.[27,28] This method allows an accurate calculation of these energies by projecting out one approximate representations of the system, obtained through a trial wave function, to its eigenstate with the lowest energy. This is accomplished by simulating a classical diffusion equation that can be identified with the Schrödinger's equation in imaginary time. An efficient exploration of the configuration space available to the system requires a guiding function for the diffusion process. An easy option for this task, though not the most efficient, is to use in the liquid phase, a guiding function of the Jastrow form

$$\Psi_J(R) = \prod_{i<j} \exp(-b/|\mathbf{r}_i - \mathbf{r}_j|)^5, \tag{6}$$

where b is a parameter adjusted to get the most efficient calculation. In the solid phase this function must be supplemented by a factor of the Nosanov form $\Pi_i \exp[-C/2(\mathbf{r}_i - \mathbf{l}_i)^2]$, a mean field term that explicitly localizes the particles about the sites $\mathbf{l}_i$ of a chosen lattice.

The simulations were performed either with the interatomic potential $V(R)$ or its two-body component $V_2(R)$. In this last case, three-body contributions to the total energies were evaluated by a perturbative method. The tail corrections of the potential energy at distances larger than half the side of the simulation cell were computed by fitting up to three damped sinusoidal functions to the two-body radial distribution function. For the three-body tail corrections we have used the Kirkwood superposition approximation $g_3(r_{12}, r_{13}, r_{23}) \approx g_2(r_{12}) g_2(r_{13}) g_2(r_{23})$.

The fitted values for the two parameters of the interatomic potential, δ and $\mathcal{A}$, were obtained through iterative least-square fits. Several hundreds of configurations of independents runs with 108 particles at different densities of the liquid and solid phases were employed to fit the energies to the experimental values. For a matter of technical convenience, the fits were done by imposing a fcc crystalline structure in the simulations of the solid phase. These calculations were performed with the interatomic potential $V(R)$. About 3000 configurations were used each time an iteration was performed. Once values of the amplitude $\mathcal{A}$ and the repulsive short-range δ parameters were obtained, fresh configurations were generated for the next iteration. We continued this procedure until the energies converged. The best values we found are $\delta = 20.352$ nm^{-1} and $\mathcal{A} = 4$.

The first observation we want to make about our results regards the nonadditivity exchange term of the three-body potential. As one might expected, it cannot be dropped if we want to keep agreement between the computed and the experimental EOS at both the liquid and solid phases. We could not get such agreement if the exchange term was neglected, i.e., by imposing $\mathcal{A} = 0$ in the fits. This is true even though the exchange contribution to the total energy is very small, as our calculations show. With respect to the damping function F of Eq. (1) the following comments are in order. Although its behavior is qualitatively similar to the corresponding function of Ref. 15, it has significant quantitative differences. It is more smooth and starts damping the triple-dipole term at distances slight larger than that of Ref. 15.

Once we have fitted the parameters δ and $\mathcal{A}$, the dependence of the computed energies on the system size was investigated both at the liquid and the hcp solid phases. The helium liquid results displayed in Table I show no indication of any size dependence. In this table we also compare results obtained through simulations obtained either with $V(R)$ or its two-body component $V_2(R)$. All of them are in excellent agreement within statistical uncertainties. The same table shows the results for the solid phase. Energies per atom computed in simulations with $N = 240$ and 180 bodies in a hcp crystalline structure are also in excellent agreement within statistical uncertainties. In both phases the error due to size effects is less than 0.01 K.

In order to verify the accuracy of the interatomic potential $V(R)$, we have computed the EOS in the liquid phase using $N = 108$ atoms. For the hcp solid the EOS was computed using 180 particles. The results at each phase were fitted to a cubic polynomial $E(\rho) = A + B[((\rho-\rho_0)/\rho_0)^2 + C(\rho-\rho_0)/\rho_0]^3$. The fits, together with experimental data, are displayed in Fig. 1. Typical values of our results are shown in Table II.

TABLE I. Size dependence of the total energy per atom of the liquid and of the hcp crystalline structure at the given densities. Calculations with $N=240$ and 180 particles were not performed in cubic simulation cells; a cube of side equal to the smallest size of the actual simulation cell would accommodate about 177 and 166 particles, respectively. Most of the simulations were performed with the V_2 potential, those with N marked with a star were done with the V potential.

ρ (nm^{-3})	N	E (K)
	Liquid	
21.86	180	-7.155 ± 0.009
	108^*	-7.171 ± 0.008
	108	-7.161 ± 0.009
25.36	180	-6.767 ± 0.009
	108^*	-6.778 ± 0.009
	108	-6.766 ± 0.009
	Solid	
30.11	240	-5.535 ± 0.01
	180	-5.538 ± 0.01
34.41	240	-3.296 ± 0.01
	180	-3.298 ± 0.01

TABLE II. Typical values of the total energy per atom at the given densities. In the last column we show experimental data from the literature (Refs. 32 and 31). At the liquid phase the simulations were performed with the $V(R)$ potential. At the highest solid density it was used as well. Other results of the hcp solid were obtained with simulations using the $V_2(R)$ potential.

ρ (nm^{-3})	E (K)	Exp. (K)
	Liquid	
21.86	-7.171 ± 0.008	-7.170[a]
23.2	-7.12 ± 0.008	-7.114
24.83	-6.897 ± 0.009	-6.893
25.36	-6.778 ± 0.009	-6.782
	Solid	
30.11	-5.538 ± 0.010	-5.56
30.88	-5.265 ± 0.010	-5.28
32.55	-4.49 ± 0.010	-4.5
34.41	-3.298 ± 0.010	-3.32
35.27	-2.68 ± 0.009	-2.68[b]

[a] Experimental value at 21.84 nm^{-3}.

[b] Interpolate from experimental data of Ref. 31.

At all densities where we have computed the total energy of the ^{4}He system, an excellent agreement between theory and experiment was found. The fitted equilibrium density $\rho_0=21.82\pm0.14$ nm^{-3} is also in agreement with experiment 21.834 nm^{-3}.[29] The melting and freezing densities are easily computed by the Maxwell double tangent construction. Our results $\rho_m=28.94\pm0.31$ nm^{-3} and $\rho_f=25.96\pm0.31$ nm^{-3} compare with the respective experimental values 28.68 nm^{-3} (Ref. 30) and 25.97 nm^{-3} (Ref. 29) in an excellent way as well.

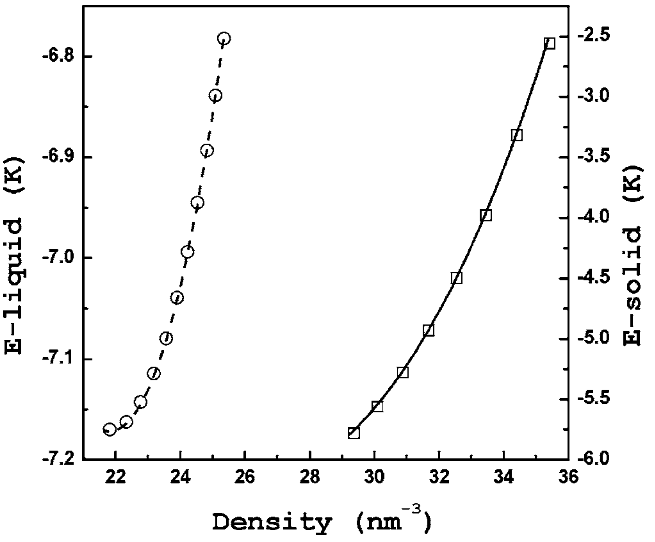

FIG. 1. Ground-state energies as a function of the density. Energy values for the liquid phase are displayed in the left side of the frame. The dashed line represents a fit of DMC results in the liquid phase. The experimental data of Ref. 32 are shown as circles. The right side of the frame show energies corresponding to the solid phase. A fit of the results for the ground-state energies in the solid phase is represented by the solid line. The squares stand for the experimental data of Ref. 31.

The energy values of the triple dipole and of the exchange interactions have been computed very accurately at two densities, one of the liquid phase and other of the hcp crystal. The calculations were performed with a multiweight DMC method.[13,16] This extension of the standard method allows the determination of the three-body contributions to the total energy to be estimated in a correlated form with the two-body energy. They were obtained without extrapolations and the results are subject only to statistical uncertainties. As our results show in Table III, the importance of the exchange term in the interatomic potential is remarkable. At the highest liquid density its contribution to the potential energy is only about 19% of the triple-dipole dispersion energy that turns out to be only 0.7% of the absolute value of the two-body potential energy. A similar behavior with respect to the intensity of these contribution is observed also at the solid phase. At the highest density we have considered in this phase the three-body exchange energy is attractive and its modulus is about 12% of the dispersion energy. In this case the contribution of the ATM term is about 1.1% of the modulus of the two-body potential energy. In other words, the biggest three-body exchange contribution we have found ac-

TABLE III. Energies per atom associated with the damped ATM and exchange V_J terms of the interatomic potential $V(R)$ at the given densities. Results were obtained with $N=108$ and 180 atoms in the liquid and solid phases, respectively.

ρ (nm^{-3})	V_{DDD} (K)	V_J (K)
25.36 (liquid)	0.175 ± 0.001	0.034 ± 0.002
35.27 (solid)	0.403 ± 0.001	-0.050 ± 0.002

counts in absolute values for less than 0.2% of the two-body potential energy.

In summary, our results have shown that it is possible to construct an interatomic potential for a system of helium atoms that very successfully describes properties of both the solid and liquid phases at same level of accuracy and in excellent agreement with experiment. This is an interatomic potential that relies on an accurate dimer potential complemented by the three-body triple-dipole term, suitably damped at short distances, and an exchange potential term with an adjusted magnitude.

The potential we are presenting in this article could be helpful in two ways. First, an accurate computation of the EOS and its associated properties always needs to be performed in the condensed phases of the systems of helium atoms. We also hope that in more detailed studies of nonaddivities, our results could be useful in the characterization of the many-body effects that play important roles in the description of these systems.

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