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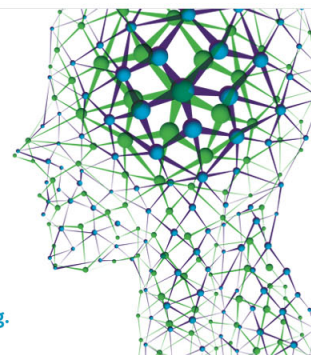
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Analysis of the contributions of three-body potentials in the equation of state of ^4He

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The effect of three-body interatomic contributions in the equation of state of ^4He are investigated. A recent two-body potential together with the Cohen and Murrell [Chem. Phys. Lett. **260**, 371 (1996)] three-body potential are applied to describe bulk helium. The triple-dipole dispersion and exchange energies are evaluated subjected only to statistical uncertainties. An extension of the diffusion Monte Carlo method is applied in order to compute very small energies differences. The results show how the three-body contributions affect the ground-state energy, the equilibrium, melting and freezing densities. © 2003 American Institute of Physics. [DOI: 10.1063/1.1611872]

I. INTRODUCTION

The unique properties of the helium systems at low temperature have attracted a continuous experimental and theoretical interest in the investigation of their ground state potential energy.¹ In the past, the construction of the best potentials used semiempirical methods where some parameters were obtained by fits to experimental data. One of them, the so-called HFDHE2 potential of Aziz and co-workers,² has allowed the understanding of many properties of helium in the condensed phases.^{3,4} Despite of small inconsistencies in this potential, it was used during a long time in these studies. It was attractive to use an effective pairwise additive potential and avoid considering high-order interactions among the atoms.

In the last decade, after a bound helium dimer was observed,^{5,6} great efforts were applied to develop *ab initio* methods in the description of He–He potentials.^{7,8} This approach was very successful. The fit⁸ of interacting energies calculated using infinite order symmetry adapted perturbation theory, Green's function Monte Carlo results and accurate dispersion coefficients to a Tang–Toennies model⁹ together with retardation added to the dipole–dipole dispersion,¹⁰ produced to date the best characterization of the helium potential energy.¹⁰

The use of very accurate two-body potential energies,^{7,8} like those offered by the *ab initio* potentials, in the investigation of bulk helium, uncovered what was known for a long time: the correct description of many of its properties in the condensed phases requires more general many-body potential. Among the many recent works where this situation was observed, we cite Refs. 11–13.

The first form of the three-body interaction considered in the study of the condensed phases of the rare gases was the one proposed by Axilrod–Teller¹⁴ and Muto.¹⁵ It was obtained by third order perturbation theory and the motivation was the calculation of the triple-dipole dispersion energy for spherical symmetric atoms. This term was used by Axilrod¹⁶

to examine the dependence of preferred crystalline structures in rare gases. The investigation of the effects of three-body exchange of electrons in trimers of helium started latter by Rosen¹⁷ using a valance bond approach. Since the work of Jansen and co-workers^{18,19} it is conjectured that three-body exchange energy is needed to understand the energy difference between the fcc and hcp crystalline structure. Many developments occurred in the investigation of nonadditive effects are reviewed in Ref. 20.

As already mentioned, the estimation of the contributions of the three-body interactions to the properties of matter in the condensed phases depend on the knowledge of accurate pair potentials. In the earlier period of the investigations of the rare gases it was assumed that the triple-dipole interactions was the only significant term beyond the two-body contributions.²¹ The inclusion of this three-body interaction improved the agreement between the experimental and theoretical values in a remarkable way.²⁰ However another important property of the solid phase, the crystal structure, remained nonunderstood.

At low temperatures, all heavier rare gases solids crystallize in a fcc lattice and only helium, when subjected to external pressure, solidify in a hcp structure. However most of the reasonable two-body potentials favor hcp over the fcc structure. The relative difference of the static potential energy is about 0.01% in favor of the hcp lattice.²² The inclusion of triple-dipole interaction still left the hcp as the more stable structure. The inclusion of higher-order terms in the dispersion energy like dipole–octopole and quadrupole–quadrupole terms did not improve agreement between theoretical results and experiment. So far, the proposed higher-order interactions greater than three-body have given no significant contributions to this question either. Recent results²³ in agreement with the early work of Jansen have shown that the inclusion of nonadditive exchange contributions are necessary to understand the preferred fcc structure of argon and its binding energy.

For the rare gases and in particular for the helium systems the largest and most well know part of the three-body interatomic potential is the triple-dipole term of Axilrod–

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Teller–Muto. The exchange contribution is less known. Despite its importance, still now, competing calculations might differ by an order of magnitude²⁴ and different potential forms could be used for fitting theoretical results obtained in calculations of the exchange energy.

Quantum Monte Carlo methods, where quantities of interest can be computed subject only to statistical uncertainties, can be very useful in the analysis and understanding of the different contributions to the potential energy. However straightforward use of these methods to compute small energies differences might not be possible. Results of independent runs and their associate statistical uncertainties might render a simple energy difference meaningless. Perturbation methods used together with quantum Monte Carlo methods still needs extrapolation²⁵ that introduces further uncertainties. Even a more sophisticated approach, based on the finite field method, might have difficulties in a situation where a small energy difference has to be computed.

The calculation of energies subject only to small statistical uncertainties (avoiding extrapolation and perturbative calculations) is not only a matter of principle but a necessity in the present case, where we have a small three-body energy and a delicate balance between its different contributions. A better understanding of the individual contributions of the three-body interactions are important by themselves and moreover can help increase the physical content of the analytical functional forms used to fit their contributions.

In this work we want to investigate in a quantitative way how a proposed representation of the three-body interaction affects the equation of state of ^4He in the liquid and solid phases and properties like the binding energy, the equilibrium, freezing and melting densities. With this aim, we describe bulk helium by employing the two-body potential of Aziz and co-workers⁷ together with the three-body potential of Cohen and Murrell.²⁶ This two-body potential continues to be widely used in the investigation of systems of helium atoms.^{27–29} The analytical expression of Cohen and Murrell has been obtained by fitting *ab initio* results of helium trimers in the isosceles geometry and seems to be the most used nowadays.^{12,24,30} In the past, the three-body potential of Bruch–McGee³¹ was also used in the investigation of the helium systems. However, the motivation of its functional form representing the electronic exchange might not be so clear and its amplitude is strongly density dependent.^{30,32,33} Our method does not depend on the form of the used potentials. It is possible and interesting to analyze quantitatively how three-body contributions will affect properties of interest of a system of helium atoms when it is described by other very accurate two-body potentials.⁸ However as our results also show, it seems more urgent to concentrate efforts in the three-body part of the potential.

To accomplish our intent of performing a quantitative study of the effects of three-body interactions in the properties of helium atoms, we have developed an extension of the diffusion Monte Carlo (DMC) method. It allows the individual calculation and analysis of the Coulomb and exchange terms of the three-body interactions without resort to a perturbative calculation followed by extrapolation. The effect of these contributions are considered in the equation of state

and quantitative results show how they affect the ground-state energy, the equilibrium, melting and freezing densities. As an additional advantage of our development we mention that it is of easy implementation and test in the available DMC codes.

The paper is organized as follows: In the next section we present the Hamiltonian together with the interacting potentials used in this work. In Sec. III we briefly describe one of the standard implementations of the diffusion Monte Carlo algorithm and our extension of this algorithm. It allows the use of a single set of walkers and reweighing to compute properties of a system of helium atoms described by different interacting potentials. Section IV contains details of our simulations; the results are presented in Sec. V. A discussion in Sec. VI concludes the work.

II. THE MODEL

The Hamiltonian we use to describe the system of helium atoms is given by

$$H = -\frac{\hbar^2}{2m}\nabla_R^2 + V(R), \quad (2.1)$$

where $R = \{\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N\}$ stands for the N coordinates of the helium atoms and $V(R)$ is the interatomic potential. In this work three sets of calculations were performed. In the first one the interatomic potential employed is an additive pairwise potential $V_2(R)$ as proposed by Aziz and co-workers.⁷ In a second set, we considered the V_{2D} potential,

$$V_{2D}(R) = V_2(R) + V_D(R), \quad (2.2)$$

obtained by adding to V_2 a damped Axilrod–Teller–Mutto^{14,15,26} triple-dipole term ($ddd \equiv D$)

$$V_D = Z^{(3)}(111) \frac{1 + 3 \cos(\gamma_1)\cos(\gamma_2)\cos(\gamma_3)}{(r_{12}r_{13}r_{23})^3} \times F(r_{12}, r_{13}, r_{23}), \quad (2.3)$$

where $Z^{(3)}(111)$ is a constant, the γ_i are the internal angles of the triangle (formed by the three particles) and the r_{ij} the lengths of its sides. The damping F is given by the product

$$F(r_{12}, r_{13}, r_{23}) = f(r_{12})f(r_{13})f(r_{23}) \quad (2.4)$$

that depends on

$$f(r_{ij}) = \begin{cases} \exp\left(-l\left(\frac{k}{r_{ij}} - 1\right)^2\right) & \text{if } r < k \\ 1 & \text{otherwise,} \end{cases} \quad (2.5)$$

where l and k are parameters. The damping of the dispersion energies at distances where charge overlap is significant is need for a reasonable description of the short range forces. The value used for $Z^{(3)}(111)$ in Eq. (2.3) is 0.324 K, as obtained by double perturbation theory.³⁴

Finally, the most complete interatomic potential we have considered,

$$V_{2DJ}(R) \equiv V_2(R) + V_D(R) + V_J(R), \quad (2.6)$$

includes contributions from the exchange potential V_J as well. The two last terms of Eq. (2.6) form the three-body

potential proposed by Cohen and Murrell.²⁶ The potential V_J is expressed through symmetry adapted coordinates Q_i (linear combinations of the three distances r_{ij})

$$\begin{aligned} Q_1 &= \frac{1}{\sqrt{3}}(r_{12} + r_{13} + r_{23}), \\ Q_2 &= \frac{1}{\sqrt{2}}(r_{13} - r_{23}), \\ Q_3 &= \frac{1}{\sqrt{6}}(2r_{12} - r_{13} - r_{23}). \end{aligned} \quad (2.7)$$

Its functional form is given by

$$\begin{aligned} V_J &= [c_0 + c_1 Q_1 + c_2 Q_1^2 + (c_3 + c_4 Q_1 + c_5 Q_1^2)(Q_2^2 + Q_3^2) \\ &\quad + (c_6 + c_7 Q_1 + c_8 Q_1^2)(Q_3^3 - 3Q_3 Q_2^2) + (c_9 + c_{10} Q_1 \\ &\quad + c_{11} Q_1^2)(Q_2^2 + Q_3^2)^2 + (c_{12} + c_{13} Q_1 + c_{14} Q_1^2)(Q_2^2 \\ &\quad + Q_3^2)(Q_3^3 - 3Q_3 Q_2^2)] \exp(-\alpha Q_1), \end{aligned} \quad (2.8)$$

that depends on parameters α and $\{c_i | i = 1, \dots, 14\}$.

III. THE DIFFUSION MONTE CARLO METHOD

A. The standard algorithm

In almost all practical implementations of the diffusion Monte Carlo method^{35,36} we compute quantities of interest by sampling the probability distribution $f_0(R) = \psi_G(R) \psi_0(R)$ that depends on $\psi_0(R)$, the true ground state wave function of the system and on a given guiding function, $\psi_G(R)$.

A careful version of this method is presented by Umrigar, Nightingale, and Runge.³⁷ A slightly simpler implementation could be described as follows. It is convenient to start the calculation with a set of configurations drawn from $|\psi_G|^2$, obtained through the Metropolis algorithm. The distribution $f_0(R)$ is sampled after an initial transient, where the excited states components are filtered. All the sampling is accomplished iteratively through the integral equation,

$$f(R, \tau) = \int dR' G_d(R, R') G_b(R, R') f(R', \tau - \Delta\tau), \quad (3.1)$$

where

$$\begin{aligned} G_d(R, R') &= (4\pi D \Delta\tau)^{-(3N/2)} \\ &\quad \times \exp\left[-\frac{(R - R' - D\Delta\tau v_D(R'))^2}{4D\Delta\tau}\right], \end{aligned} \quad (3.2)$$

$$D = \frac{\hbar^2}{2m}, \quad v_D = 2\nabla \ln \Psi_G, \quad (3.3)$$

$$G_b(R, R') = \exp\left\{-\left(\frac{\Delta\tau}{2}\right)[E_L(R) + E_L(R')] + \Delta\tau E_T\right\}. \quad (3.4)$$

Here, E_T is a trial energy and E_L is the local energy given by

$$E_L = H\Psi_G/\Psi_G; \quad (3.5)$$

$f(R, \tau)$ for a long enough τ goes to $f_0(R)$.

It is correct to write the Green's function as the product of Eq. (3.1) only up to $\mathcal{O}(\tau^3)$. This implies that to obtain exact results, within statistical fluctuations, short times $\Delta\tau$ must be used in the iterations and an extrapolation to $\Delta\tau \rightarrow 0$ performed (see however comments in Sec. IV). This is the so-called short-time approximation. The value of $\Delta\tau$ is a parameter of the calculation.

Each configuration undergoes three steps: drift, diffusion, and branching. Very frequently a single configuration is called a walker and an iteration of all walkers a generation. For the drift step we need to compute the quantum velocity v_D . In the second step the configuration diffuses. This is accomplished by sampling G_d . Accordingly, a walker in R' is propagated during a time step $\Delta\tau$ to its new point R through

$$R = R' + \chi + D\Delta\tau v_D(R'), \quad (3.6)$$

where χ are normal deviates of a Gaussian function with variance $2D\Delta\tau$ and zero mean.

To propagate a walker, we can change all the particle's coordinates at once or those of a single particle at a time. In this last case we perform N updates to propagate each walker. To improve^{36,38} the approximation of the Green's function, we only accept moves with probability

$$p_{\text{accept}}(R' \rightarrow R) = \min\left[1, \frac{G_d(R', R)\Psi_G^2(R)}{G_d(R, R')\Psi_G^2(R')}\right] \quad (3.7)$$

and chose $\Delta\tau$ such that more than 99% of the attempted moves are accepted. This condition imposes detailed balance on the splitted Green's function and restores this property of the exact Green's function. Regardless of the time step, it guarantees also a correct sampling if hypothetically we could use as ψ_G the exact ground state wave function. In such case, this implementation of the DMC method reduces to a variational Monte Carlo calculation with trial moves sampled from G_d .

To complete the iteration of Eq. (3.1), we compute G_b considered as a weight for the walker. At the begin of the simulation, all the walker's weights are assumed to be equal to one. In order to minimize fluctuations in G_b , an effective time step is used.^{36,37} It is given by $\Delta\tau_{\text{eff}} = \Delta\tau(\Delta\rho_d^2/\Delta\rho^2)$, where $\Delta\rho^2$ is the mean square displacement of all proposed moves in the diffusion step and $\Delta\rho_a^2$ is the related quantity when only accepted moves are considered. Finally the weight w' of the walker is updated to its new value w according to

$$w = w' G_b(R, R'). \quad (3.8)$$

After propagating all walkers we have a new generation and a sample of the probability distribution f as an weighted average over the walkers. For reasons of efficiency the number of configurations used in the estimation of $f(R)$ fluctuates according to the following branching rules. If w is greater than 2, the walker is duplicate and each one will carry half of its weight. On the other hand if two walkers, R_i and R_j , have weights less than 0.5, only one survives with a weight given by $w_i + w_j$. The decision of which one will

survive is made by sampling $r = w_i / (w_i + w_j)$. That is, we draw a random number ξ and compare it with r . If r is small than ξ we keep configuration R_j , otherwise R_i is kept. If the weight computed by Eq. (3.8) lies between 0.5 and 2, a single copy of the walker with weight w is kept. The values of the weights where the branching is performed certainly could be changed, we only need rules that neither introduce bias or result in a scheme too inefficient.

Once a generation has been completed, quantities of interest like the energy, can be computed as

$$E_m = \frac{\sum_i w(R_i) E_L(R_i)}{\sum_i w(R_i)}, \quad (3.9)$$

where the sum is performed over all the walkers of a given generation. Usually for reasons of efficiency, one uses sparse average to estimate the quantities of interest. Only a fraction of the generations are employed to compute these quantities. This is done to decrease the correlation between estimates. This procedure together with block averages of the energies $\{E_m\}$ are the most efficient way of obtaining the final estimate of the energy and its variance.

The number of walkers is controlled by adjusting the value of E_T . This number is kept roughly constant. We have experienced with both heuristic and automatic changes of E_T as given by

$$E_T = E_0 + \kappa \ln(T_p / C_p), \quad (3.10)$$

where κ is a parameter, T_p is the target population and C_p the current population. For our purposes, the results were equivalent for both methods of changing E_T . Adjustments in E_T were gentle and were not made more frequently than once every 20 generations.

It is well known^{36,39} that estimates of the quantities of interest like the energy in Eq. (3.9) are biased. The source of bias are due to both: population control and because the expected value of a quotient is not the quotient of the expected values. So the determination of useful results require the evaluation of the bias or at least to have its magnitude bounded. The bias can be reduced by increasing the size of the population. We have observed that for a system of helium atoms, where simulations with 108/64 bodies are easily performed, a population of about 400 walkers give results where errors due to the bias are smaller than the statistical ones. Certainly, more sophisticated methods^{37,40} of bias suppressing could be applied as well.

B. The algorithm with reweighing

In many situations it is interesting to compute energies differences resulting from different interatomic potentials. However it is not always possible to simply use results from independent runs to obtain such differences. If they are small, statistical fluctuations might well produce errors that are bigger than these differences themselves, rendering the result meaningless. It is however possible to modify the DMC method in such a way that the same set of walkers are used to compute quantities of interest associated to the different potentials we want to investigate. The energies that are obtained are correlated and thus more meaningful differences

can be computed. No approximations are introduced. If the actual interest is on the energies, it is not necessary to use extrapolated estimators either. What we are proposing is to sample different probabilities distributions functions, associated to the different interatomic potentials we want to investigate, by using the same set of walkers with appropriate weights. As just mentioned, the values of the quantities of interest obtained are correlated and the errors associate with their difference reduced by orders of magnitude. We want to call attention to the fact. Although our method relies on a set of weights, it cannot be related to the forward walking⁴¹ or reptation⁴² methods. For every generation of equilibrated walkers, we can compute the quantities of interest without any further propagation. Moreover the weights we have for a given walker are associated with different interatomic potentials.

In our modified DMC method, to each walker we attach a set of weights, one for each potential we want to consider. In our implementation of the algorithm we have attached three different weights for each walker, one for each of the three different interatomic potentials used. Of course this number in the method is arbitrary. It was chosen because of the specific aspects of many-body interactions in the interatomic potential we want to investigate. It would be possible to use only two weights or any other convenient number of weights.

As in the standard algorithm, the calculations start with a set of walkers draw from $|\psi_G|^2$. Since a single guide function is use, the drift and diffusion steps are performed exactly as before. We compute the drift velocity v_D , generate the normal distribution of variates, update R according to Eq. (3.6), and accept it with probability p_{accept} of Eq. (3.7). In the present algorithm, we sample the three different probabilities distributions in which we are interested by completing the iteration considering three different $G_b^{(k)}$, and updating the weights as follows:

To be specific let us consider a single walker just propagated to a new configuration R . One of its weights, $w^{(2)}$ is associate with the local energies $E_L^{(2)}(R)$ computed using only the Aziz two-body potential V_2 in the Hamiltonian of Eq. (2.1). The weight $w^{(2)}$ is updated according to Eq. (3.8) by evaluating $G_b^{(2)}$ of Eq. (3.4) using the local energy $E_L^{(2)}(R)$. Another weight of the same walker, $w^{(2D)}$ is calculated with the local energy $E_L^{(2D)}(R)$ computed with the Hamiltonian that uses the V_{2D} potential of Eq. (2.2), it includes the triple-dipole contributions to the two-body potential. The calculation of the new value of $w^{(2D)}$ for this walker proceeds as before. $G_b^{(2D)}$ in Eq. (3.4) is evaluated employing $E_L^{(2D)}(R)$ and the update finished according to Eq. (3.8). The third weight, $w^{(2DJ)}$, is associated with the interatomic potential that also includes exchange contributions. It is computed by considering $E_L^{(2DJ)}(R)$ that depends on the Hamiltonian that uses the full potential V_{2DJ} of Eq. (2.6). The update of $w^{(2DJ)}$ is performed along the exact same lines already described for the other weights. The different values of the weights are due only to the local energy used in their computation, i.e., to the interatomic potential employed. We remember again that the same configuration is used to compute these three weights.

After propagating all walkers, a new generation will finally be obtained by using the following branching rules. When $\min(w^{(2)}, w^{(2D)}, w^{(2DJ)})$ is large than 2 the walker is duplicated and each one of the copies will carry half of the value of the weights: $(w^{(2)}/2, w^{(2D)}/2, w^{(2DJ)}/2)$. If two walkers, i and j have weights such that $\max(w_i^{(2)}, w_i^{(2D)}, w_i^{(2DJ)})$ and $\max(w_j^{(2)}, w_j^{(2D)}, w_j^{(2DJ)})$ are less than 0.3, we consider each kind of weight individually. We draw a single random number ξ and make comparisons of ξ with $r^{(2)}$, $r^{(2D)}$, and $r^{(2DJ)}$, where $r^{(k)} = w_i^{(k)} / (w_i^{(k)} + w_j^{(k)})$. Three situations might happen: (i) in all the comparisons ξ is smaller than $r^{(k)}$, then we keep walker i with weights $\{w_i^{(2)} + w_j^{(2)}, w_i^{(2D)} + w_j^{(2D)}, w_i^{(2DJ)} + w_j^{(2DJ)}\}$ and discard walker j ; (ii) always ξ is greater than $r^{(k)}$, in this case we keep R_j with the same sum of weights as above and discard R_i ; (iii) one of the comparisons favors a walker different from the other two. For definiteness let say that ξ is smaller than $r^{(2)}$ and greater than $r^{(2D)}$ and $r^{(2DJ)}$. In this case we will keep the two walkers, R_i with weights $\{w_i^{(2)} + w_j^{(2)}, 0, 0\}$ and R_j with weights $\{0, w_i^{(2D)} + w_j^{(2D)}, w_i^{(2DJ)} + w_j^{(2DJ)}\}$. These new weights are telling us that in fact we have deleted walker i from the calculations with the interatomic potential that includes three-body interactions and walker j when we are considering only the two-body potential. This is a bad situation in the sense that we are introducing two walkers in the calculations that will not give anymore the correlations that we are looking for. Fortunately, if needed, the cases where this situation happens can be systematically reduced in a simple way. It is enough to decrease the threshold value used to combine walkers (see Sec. IV). If one of the weights of a walker lies between 0.3 and 2, a single copy is maintained with weights $(w^{(2)}, w^{(2D)}, w^{(2DJ)})$.

Each one of the calculations we are performing must give within statistical fluctuations the results obtained by the standard algorithm. This makes very easy to test the code. Each new potential introduced give results that can immediately be tested against the standard implementation of the algorithm. The computational cost of our modification of the standard algorithm is very small, it amounts basically to the calculation of a new term of the potential energy.

Periodically, about one every four or five generations we compute several quantities of interest. Evaluations of the energies $E_m^{(2)}$, $E_m^{(2D)}$, and $E_m^{(2DJ)}$ in a given generation are readily obtained by including all the walkers i it has

$$E_m^{(k)} = \frac{\sum_i w_i^{(k)}(R_i) E_L^{(k)}(R_i)}{\sum_i w_i^{(k)}(R_i)} \quad (k=2, 2D, 2DJ), \quad (3.11)$$

in this expression, m denotes one of the estimates in the sequence $\{E_m^{(k)}\}$. Together with these quantities, we have also evaluated the energy associate to the damped triple-dipole term in the interatomic potential by

$$E_m^{(D)} = E_m^{(2D)} - E_m^{(2)}, \quad (3.12)$$

and the energy associate with the exchange term V_J by

$$E_m^{(J)} = E_m^{(2DJ)} - E_m^{(2D)}. \quad (3.13)$$

As already mentioned, the computation of these values are straightforward because we have already estimates of the en-

ergies $E_m^{(k)}$. Along the runs, block averages of the quantities $(E_m^{(2)}, E_m^{(2D)}, E_m^{(2DJ)}, E_m^{(D)}, E_m^{(J)})$ are formed and their estimates and associate errors obtained.

Since each one of our results for $E^{(2)}$, $E^{(2D)}$ and $E^{(2DJ)}$ are completely equivalent to those that could be obtained using the standard algorithm, the observation regarding the bias of these results are in order. However we stress that the differences $E^{(D)}$ and $E^{(J)}$ should have errors that are smaller than $E^{(2)}$, $E^{(2D)}$ or $E^{(2DJ)}$.

IV. THE SIMULATIONS

In the investigation of the properties of bulk helium we impose periodic boundary conditions. The cutoff convention, the distance beyond which a potential is set to zero, is enforced for all interactions at half of the box size, $L/2$. Distances between pairs of particles are computed by the minimum-image convention. When considering three-body interatomic interactions, the length of the third side of the triangles formed by the particles cannot in general be computed using the minimum-image convention. A modification needs to be introduced so that the length of this side can be computed in a proper way and discarded if greater than $L/2$. To be specific let us consider particles i , j , and k . We compute distances r_{ij} and r_{ik} using the minimum-image convention. The difference in the x coordinates of the associated particles are

$$\begin{aligned} x_{ij} &= x_i - x_j - t_{ij}, \\ x_{ik} &= x_i - x_k - t_{ik}, \end{aligned} \quad (4.1)$$

where the translation vector t is defined as

$$t_{lm} = [(x_l - x_m)/L]L$$

and $[x]$ is the closest integer to x . If the difference x_{jk} of the third side is computed as⁴³

$$x_{jk} = x_j - x_k + t_{ij} - t_{ik}, \quad (4.2)$$

it is not hard to see that all possibilities in the simulation box are taken into account and the right value of the distance can be obtained. If this value is little than $L/2$ the calculation for this triangle proceeds. For the y and z coordinates a similar approach is used and then the three-body interaction is computed if all sides for this triangle are smaller than $L/2$. The calculation continues until all triangles have been considered.

The diffusion Monte Carlo calculations started with an initial set of 400 configurations, previously draw from $|\psi_G|^2$ using the Metropolis algorithm. Before accumulating quantities of interest the excited states components of our ensemble of configurations are filtered by performing several iterations of Eq. (3.1). This process takes typically of the order of 400 generations, and depends on the system density. The accumulation of the quantities of interest started after plots of the configurations energies versus Monte Carlo time steps have shown converged results for all these quantities.

We study the liquid phase using a guiding function of the Jastrow form,

$$\Psi_J(R) = \prod_{i < j} f(r_{ij}), \quad (4.3)$$

where the factor $f(r_{ij}) = \exp(-u(r_{ij})/2)$ explicitly correlates pairs of particles through a pseudopotential of the McMillan form $u(r_{ij}) = (b/r_{ij})^5$; b is a parameter.

For the solid phase we have used a Nosanov–Jastrow guiding function

$$\Psi_{NJ}(R) = \Psi_J(R)\Phi(R), \quad (4.4)$$

where

$$\Phi(R) = \prod_i \exp\left[\frac{C}{2} - (\mathbf{r}_i - \mathbf{l}_i)^2\right] \quad (4.5)$$

is a mean field term that localizes the particles around the given lattice sites \mathbf{l}_i .

All guiding functions were previously optimized by performing variational calculations. Although this is a convenient way of obtaining the values of the parameters, in principle they could be obtained without performing such calculations. It would be enough to choose parameters values that give the fastest filtering of the excited states of the initial configurations. The guiding functions used in this work, Eq. (4.3) and Eqs. (4.4)–(4.5), have been previously successfully used in Green’s function Monte Carlo calculations.³

The time steps $\Delta\tau$ used in the calculations depends on the density. Their values vary within the range 0.001–0.002 (K^{-1}) in order to obtain more than 99% of acceptance of the attempted moves. We also observed that at this acceptance level, the extrapolation to $\Delta\tau \rightarrow 0$ of the energies values were in excellent agreement, within statistical fluctuations, to the actual values obtained in the calculation itself.

The quantities reported in this work were obtained by forming averages with about 500 estimates. Each estimate was performed after four generations. Blocking was used in order to avoid correlations in the calculations of the variances. After the initial transient we typically have 550 configurations and they do not fluctuate by more than 5%.

We have considered systems with 108 particles in the solid phase. In the liquid phase we have considered 64 particles. At the equilibrium density, $\rho_0 = 21.86 \text{ nm}^{-3}$, to estimate size effects we have also performed simulations with 108 particles. Tail corrections of the two-body potential energy were made by assuming a pair distribution function equal to one beyond half the size of the simulation cell and integrating the potential up to infinity. No tail corrections were performed for the high-order interactions. For the Axilrod–Teller interaction, the tail correction is less than 7% of its value at $\rho_0 = 21.86 \text{ nm}^{-3}$ (see next section and Table II). This value is in rough agreement with a previous estimate of this quantity.⁴⁴ For the exchange energy the relative tail correction is bigger than the one of the dispersion energy. However it should remain within the statistical uncertainty of our results (see Tables I and II).

The situation where we have a walkers with one of its weights equal to zero destroys the correlation we want to construct. If we combine walkers when all their weights is less or equal 0.3, we noticed that the number of walkers with at least one of weights equal zero does not exceed 2% of

TABLE I. Total energies per atom in units of K obtained at the given densities and potentials. Results in the second column for the potential V_2 , in the third and fourth columns the V_{2D} and V_{2DJ} potentials were considered (see text). In the liquid phase the results were obtained with 64 bodies and in the solid phase with 108 particles. In the last column we show the experimental values.

ρ (nm^{-3})	$E^{(2)}$	$E^{(2D)}$	$E^{(2DJ)}$	Expt.
Liquid				
19.64	-7.121 ± 0.006	-7.016 ± 0.006	-7.011 ± 0.006	-7.01^b
21.86	-7.238 ± 0.009	-7.103 ± 0.010	-7.097 ± 0.010	-7.14^b
21.86 ^a	-7.240 ± 0.007	-7.101 ± 0.007	-7.095 ± 0.007	-7.14^b
24.01	-7.120 ± 0.010	-6.949 ± 0.010	-6.942 ± 0.010	-7.00^b
26.23	-6.541 ± 0.014	-6.325 ± 0.014	-6.318 ± 0.014	-6.53^b
Solid				
29.34	-5.907 ± 0.004	-5.600 ± 0.003	-5.600 ± 0.004	-5.78^c
32.88	-4.489 ± 0.006	-4.071 ± 0.006	-4.076 ± 0.007	-4.32^c
33.54	-4.089 ± 0.005	-3.648 ± 0.005	-3.656 ± 0.005	-3.94^c
35.27	-2.831 ± 0.006	-2.323 ± 0.006	-2.336 ± 0.006	-2.70^c

^aResult for 108 particles.

^bReference 45.

^cReference 49.

their total number. If needed this fraction can be further and systematically reduced by using a threshold smaller than 0.3 to combine walkers. As we have observed, this is done at expense of a less efficient calculation. We have concluded that the threshold 0.3 for combination of walkers is perfectly reasonable for our purposes.

V. RESULTS

A. Liquid phase

We conducted several independent runs at four different densities ρ of liquid helium, 19.64 nm^{-3} , at the experimental equilibrium density $\rho_0 = 21.86 \text{ nm}^{-3}$, 24.01 nm^{-3} , and at 26.23 nm^{-3} . In Table I are shown the total energies obtained using the two-body potential V_2 , the V_{2D} potential of Eq. (2.2), the V_2 potential plus the Axilrod–Teller term, and the V_{2DJ} potential of Eq. (2.6), the exchange term added to the V_{2D} potential. Note that at any given density, a single set of walkers is used to compute the energies associated to each one of the potentials and so these energies are correlated. We can believe that the results show their evolution as more elaborated interacting potentials are used, despite the statistical uncertainties in the results.

In Table II we shown very accurate calculations of the Axilrod–Teller and exchange energies at these four densities. For comparison we show also extrapolated results of perturbative calculations performed using configurations generated with the V_2 potential. We have plot these results in Figs. 1 and 2. The Axilrod–Teller energies calculated using reweighting are greater than the extrapolated perturbative results. Moreover they do not always agree within the statistical uncertainty. The triple-dipole interaction gives a positive contribution to the energy of the system and its value double when we go from the lowest to the highest density.

The energies due to the exchange term in the V_{2DJ} potential when calculated with respect to the total energies obtained with the V_{2D} potential are on average about 0.0010 K smaller than the extrapolated perturbative results. In addition

TABLE II. Energies per particle in units of K associated with the triple-dipole term (E^D) and the exchange term (E^J) at the given densities obtained by reweighing and by extrapolation of the perturbative calculation.

ρ (nm $^{-3}$)	E^D		E^J	
	Rew.	Extr.	Rew.	Extr.
Liquid				
19.64	0.105 \pm 0.001	0.1012 \pm 0.0002	0.0044 \pm 0.0003	0.0056 \pm 0.0001
21.86	0.135 \pm 0.001	0.1333 \pm 0.0002	0.0056 \pm 0.0004	0.0066 \pm 0.0001
21.86 ^a	0.139 \pm 0.002	0.1351 \pm 0.0006	0.0058 \pm 0.0004	0.0068 \pm 0.0001
24.01	0.171 \pm 0.001	0.1698 \pm 0.0002	0.0063 \pm 0.0003	0.0074 \pm 0.0001
26.23	0.217 \pm 0.001	0.2136 \pm 0.0002	0.0069 \pm 0.0005	0.0078 \pm 0.0001
Solid				
29.34	0.307 \pm 0.001	0.3035 \pm 0.0002	0.0000 \pm 0.0003	0.0019 \pm 0.0001
32.88	0.418 \pm 0.001	0.4140 \pm 0.0002	-0.0051 \pm 0.0007	-0.0028 \pm 0.0002
33.54	0.441 \pm 0.001	0.4379 \pm 0.0002	-0.0072 \pm 0.0008	-0.0050 \pm 0.0002
35.27	0.508 \pm 0.001	0.5029 \pm 0.0002	-0.0128 \pm 0.0006	-0.0097 \pm 0.0002

^aResult for 108 particles.

there is no agreement within statistical uncertainties between the energies calculated with the reweighing and perturbative methods at $\rho=19.64$ and $\rho=24.01$ nm $^{-3}$. The energies calculated using reweighing are lower than the extrapolated perturbative results, contrary to what happens with the triple-dipole interaction. The exchange energy is also positive at all densities examined and increases with it. At the highest density it is approximately 50% greater than in the lowest one.

B. Solid phase

For the solid phase we have considered four densities: 29.34, 32.88, 33.54, and 35.27 nm $^{-3}$. In Table I are shown the total energies, obtained with a systems of 108 particles in a fcc structure. Again, we have considered the potentials V_2 , V_{2D} , and V_{2DJ} . Table II shows our very accurate results of

the Axilrod–Teller and exchange contributions to the potential energy and also extrapolated perturbative results for comparison. The difference is about the same we have observed in the liquid phase. For the Axilrod–Teller term they do not agree within the statistical uncertainty at ρ equal to 32.88 and 35.27 nm $^{-3}$. In this phase as well, the Axilrod–Teller energies computed by reweighing are greater than the corresponding extrapolated perturbative results, and they remain positive. They also increase with the density. At the highest density (35.27 nm $^{-3}$) it is 60% greater than in the lowest one.

The contribution of the exchange term in the solid region is null or negative and differs significantly from the perturbative results. At the lowest density (29.34 nm $^{-3}$) the result obtained by reweighing gives a null contribution while the extrapolated perturbative quantity is positive. In the other

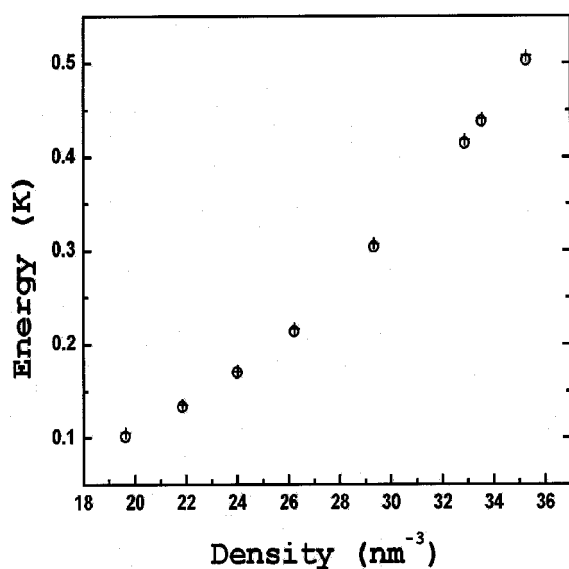


FIG. 1. Energy per atom associated with the three-body Axilrod–Teller interaction term for the liquid and solid phases. The crosses stand for the DMC results with reweighing. The circles show extrapolated estimates of perturbative calculations. The statistical errors are smaller than the size of the symbols. The results were obtained using a simulation cell with 64 particles for the liquid phase and 108 for the solid one.

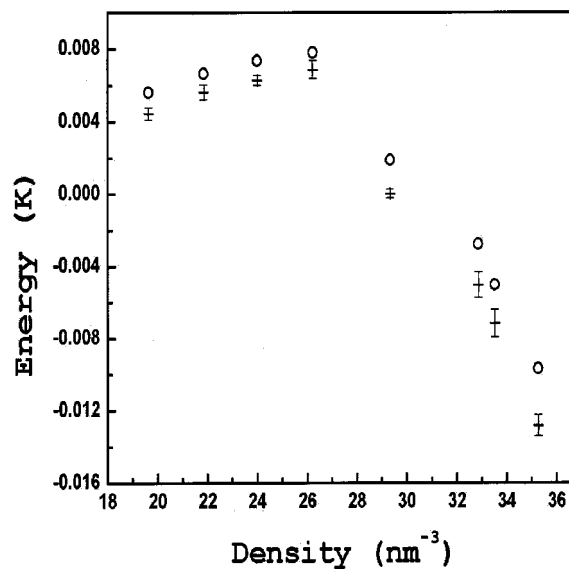


FIG. 2. Energy per particle associated with the three-body exchange term for the liquid and solid phases, DMC with reweighing (crosses) and extrapolated perturbative results (circles). The statistical errors of the last calculations are smaller than the size of the symbols. The results were obtained using a simulation cell with 64 particles for the liquid phase and 108 for the solid one.

TABLE III. Fitting parameters of the liquid and solid equations of state for three different potentials. In the first line, for both the liquid and solid phase, the two-body potential V_2 of Aziz *et al.* (Ref. 7) was used. Then we present results when the three-body Axilrod–Teller term is included in the interacting potential, V_{2D} . In the rows with V_{2DJ} we show results obtained when the full potential, that includes the three-body exchange term in V_{2D} , was used. The experimental value of the equilibrium density is also presented. The units of E_0 , B , and C are expressed in K.

Potential	ρ_0 (nm^{-3})	E_0	B	C
Liquid				
V_2	22.133	-7.240	13.549	37.025
V_{2D}	21.845	-7.103	12.143	35.705
V_{2DJ}	21.834	-7.097	12.081	35.480
Expt.	21.85 ^a			
Solid				
V_2	26.795	-6.200	31.880	5.661
V_{2D}	26.399	-5.980	29.739	7.870
V_{2DJ}	26.045	-6.028	25.233	11.844

^aReference 46.

densities the exchange energy computed by reweighing continues to be lower than the corresponding extrapolated perturbative values that are negative. In the solid phase the relative variation of the exchange energy is greater than the corresponding quantity for the Axilrod–Teller energy.

C. Melting–freezing transition

The calculations of the melting and freezing densities were performed by a Maxwell double-tangent construction in analytical equations of state for the liquid and crystalline phases. The equations were determined by fits of our results to functions of the form,

$$E(\rho) = E_0 + B \left(\frac{\rho - \rho_0}{\rho_0} \right)^2 + C \left(\frac{\rho - \rho_0}{\rho_0} \right)^3. \quad (5.1)$$

This functional form has been extensively used in the literature, including to fit experimental equation of state.^{45,46} We have fitted equations of state using results from the three different potentials, V_2 , V_{2D} , and V_{2DJ} . The fitted parameters, E_0 , B , C , and ρ_0 in the liquid and solid phases are presented in Table III. In Fig. 3 we plot the equations of state.

The freezing and melting densities determined by the Maxwell double tangent construction are listed in Table IV. Looking at this table, we can follow the changes in the freezing and melting densities as more elaborated interacting potentials are used. The computed freezing densities differs, about 3% from the experimental value. This difference is of about 4% for the melting densities. The calculated freezing densities are below the experimental value, contrary to the computed melting densities that are above the experimental value.

VI. DISCUSSION

In this work we are able to verify without any approximations how small changes in the interacting potential affects some of the properties of bulk helium. It was possible to analyze in a quantitative way how the Axilrod–Teller and the exchange three-body contributions to the interatomic po-

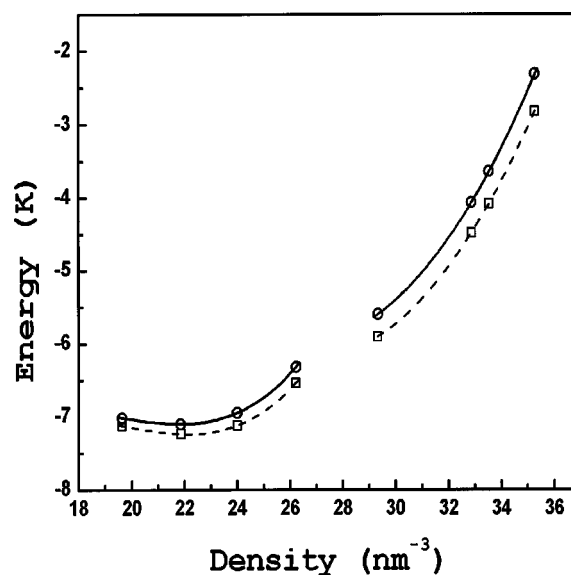


FIG. 3. Analytical equations of state with three different potentials for the solid and liquid phases. The dashed line represent the equation of state obtained using the results determined with the two-body potential V_2 . The solid line represent results using the V_{2D} and V_{2DJ} potentials that includes only the Axilrod–Teller term and this term plus the exchange one, respectively. At the figure scale the two last fits are indistinguishable. The squares and circles represent results from our calculations.

tential modify the equation of state of this system. This was accomplished by a DMC calculation where a single set of walkers was used. Thus the quantities of interest associate with the different potentials were obtained in a correlated fashion and so despite of the statistical errors their difference are meaningful.

The comparison between the total energy per atom obtained with a very accurate two-body potential and the experimental values made in Table I show that high-order terms in the description of the atomic interaction are needed. In the same token, as the contributions of the dispersion energy are much better known than those of the exchange energy, the results suggest that more efforts would be desirable in developing reliable ways of computing the energies associated to this last kind of interaction.

The results of the Axilrod–Teller triple-dipole dispersion energy and of the three-body exchange energy as a function of the density reported in Table II, Figs. 1 and 2, show qualitative agreement between our method and the usual approach

TABLE IV. Melting and freezing densities using three different potentials calculated by the Maxwell double tangent construction method. The V_2 potential is the two-body potential of Aziz *et al.* (Ref. 7). The V_{2D} potential is build using the V_2 potential plus the three-body Axilrod–Teller interaction term. Finally the V_{2DJ} potential includes the V_2 potential, the three-body Axilrod–Teller, and the exchange terms. In the last line we give the experimental values.

Potential	ρ_f (nm^{-3})	ρ_m (nm^{-3})
V_2	24.94	29.39
V_{2D}	25.00	29.35
V_{2DJ}	24.99	29.28
Expt.	25.8 ^a	28.0 ^a

^aReference 50.

of extrapolating perturbative calculations. However this last method can not be trusted in giving the right magnitude of the three-body energies. In some cases the results do not agree within statistical uncertainty with those obtained using reweighing. Unfortunately since those cases can not be identified in advance, it will remain doubts over all results obtained with extrapolated perturbative calculations of the three-body contributions to the potential energy. Although better functions, for instance with explicit triplet correlations, could mitigate the difficulties associate with the extrapolation, it would require more evolved programing and elaborate trial function optimizations.

As expected, our results show that in both liquid and solid phases, the Axilrod–Teller term gives more important energy contribution to the total energy than the exchange term. It is also interesting to note that at the lowest solid density we have considered (29.34 nm^{-3}), the extrapolated perturbative result associated with the exchange term gives a positive energy contribution whereas the value obtained by reweighing is null.

Although the inclusion of the three-body interaction potentials used in this paper did not bring agreement with the experimental values of the melting and freezing densities, it is important to note that our calculations show that the inclusion of the triple-dipole and the exchange terms, as proposed by Cohen and Murell,²⁶ are leading the melting and freezing densities to their right values, cf. Table IV. All the small differences we observe in these quantities are within their estimated error (0.2 nm^{-3}). However since we used a single set of walkers to compute them, we can trust that their relative difference are significant in our calculations.

It is also important to contrast our results with those obtained with an equation of state determined using extrapolated perturbative calculations. Although the freezing density calculated by this last method practically follows our results, the value obtained with this method for the melting density is almost constant and equal to 29.29 nm^{-3} , independently of the potential used. This last result could lead to the false conclusion that three-body interactions does not affect this property.

Other consequence of including many-body interactions in the potential can be seen in the calculation of the equilibrium density [Table III, Eq. (5.1)]. For both potentials, V_{2D} and V_{2DJ} , the theoretical computed value of the equilibrium density becomes almost identical to the experimental value. The equilibrium density obtained using the full interatomic potential V_{2DJ} diminished 0.3 nm^{-3} from its value computed with the two-body potential. In the solid phase, in which the contribution of the exchange energy is greater, the parameter ρ_0 decreases 0.75 nm^{-3} in a similar comparison.

The theoretical determination of a realistic equation of state of ^4He requires an accurate two-body potential (like the one we use⁷ or the one⁸ employed in Ref. 12) together with three-body terms.²⁶ Further understanding of these interactions requires²⁴ a quantitative discrimination of their different contributions to the properties of the system. In this work by introducing reweight in a DMC calculation we can follow how each term of the three-body interaction used affects the

binding energy, the equilibrium, freezing and melting densities.

The reweight method we have presented here can in principle be used to evaluate expectation values $\langle A \rangle$ of local operators A , operators that depend only on the coordinates and so that can be incorporated to the potential energy. Our method can also be thought as complementary to the finite field method use in conjunction with DMC. In this method a term of the form (δA) is added to the Hamiltonian and the value of $\langle A \rangle$ is obtained by determining the slope of $E(\delta)$ computed in a series of different runs. Our method could be used to calculated all these $E(\delta)$ in a single run. Since the $E(\delta)$ are correlated, the slope of its plot as a function of δ , the expectation $\langle A \rangle$, will be obtained more easily. If the amplitude of the operator A is small, like those we have in this work, the linear response approach most probably becomes too noise and it would be necessary to use our method. For nonlocal operators, like the kinetic energy of a component in a multicomponent system, it would be very interesting to learn if it is possible within the linear response approach of Ref. 48 to assume that the diffusion does not change for the different values of δ . If this is true, them always would be advantageous to use the finite field approach together with our method.

The extension we have proposed to the DMC method might be very useful not only for the helium systems, but also for other quantum many-body systems where a clue is need to identify the best description between competing interacting potentials. Even if these potentials differ by very small amounts, the nature of the interactions they describe can be different. A better understanding of these differences and their relevance is important on its own and so as mean of obtain better analytical representations of the interacting potentials. The calculations of small energy contributions of spin–orbit terms in molecular physics⁴⁷ might be another situation where our method can help in better understanding a physical system.

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