Thermal Helium Clusters at 3.2 Kelvin in Classical and Semiclassical Simulations

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The thermodynamic stability of $^4He_{4-13}$ at 3.2 K is investigated with the classical Monte Carlo method, with the semiclassical path-integral Monte Carlo (PIMC) method, and with the semiclassical all-order many-body method. In the all-order many-body simulation the dipole–dipole approximation including short-range correction is used. The resulting stability plots are discussed and related to recent TOF experiments by Stephens and King. It is found that with classical Monte Carlo of course the characteristics of the measured mass spectrum cannot be resolved. With PIMC, switching on more and more quantum mechanics by raising the number of virtual time steps results in more structure in the stability plot, but this did not lead to sufficient agreement with the TOF experiment. Only the all-order many-body method resolved the characteristic structures of the measured mass spectrum, including magic numbers. The result shows the influence of quantum statistics and quantum mechanics on the stability of small neutral helium clusters.

KEY WORDS: Helium; cluster; quantum mechanics; quantum statistics; simulation; many-body; path integration.

The most common modeling methods applied to finite-temperature atomic clusters are Monte Carlo, molecular dynamics, and combinations of both. Little work has been done on critically comparing those simulation techniques, i.e., comparing the relevance of physical assumptions of a particular system with respect to the simulation model that is used. Thus, in this paper three Monte Carlo simulations of ^4He_n clusters (n is the number of atoms) are studied. The results of classical Monte Carlo simulation, the semiclassical path integral Monte Carlo (PIMC) simulation based on the quantum statistical motion of the particles, and the semiclassical all-order

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many-body Monte-Carlo simulation based on the quantum mechanical many-body dispersion interaction are discussed.

The simulation of the quantum statistical motion of $^4\mathrm{He}_n$ clusters has been carried out with the path integral Monte Carlo (PIMC) method[1] with 257 virtual time steps. The simulation of classical $^4\mathrm{He}_n$ clusters run with the trivial application of the PIMC algorithm, i.e., with zero virtual time steps. As a model potential for both the classical and the PIMC simulation, the two-body Lennard-Jones (12, 6) potential is used,

$$U = U_{\mathrm{LJ}} = \sum_{i>j} 4\varepsilon \left[\left(\frac{\sigma}{r_{ij}}\right)^{12} - \left(\frac{\sigma}{r_{ij}}\right)^{6} \right] \tag{1}$$

with the LJ parameters $\sigma = 2.556$ Å and $\varepsilon/k_{\mathrm{B}} = 10.22$ K.

The simulation of many-body interactions in $^4\mathrm{He}_n$ clusters was carried out with the zero-virtual-timestep PIMC and a dispersion many-body correction. It enters with the interaction of the static atomic polarizabilities $\alpha = \alpha(r)$ of the helium atoms and the resulting effective atomic polarizability α_{eff}, respectively. The atomic polarizability is determined by a $^4\mathrm{He}_2$ two-body exchange calculation of Heller *et al.*[4] It was fitted to the data by Heller *et al.* with Dacre's polarizability function[3]

$$\alpha(r) = A_6 r^{-6} - t_0 \exp[-(r - \sigma_{\mathrm{F}})/r_t] \tag{2}$$

The resulting coefficients are $A_6 = -400.06 a_0^9$, $t_0 = 0.3237 a_0^3$, $\sigma_{\mathrm{F}} = 3.10 a_0$, and $r_t = 0.50 a_0$ (r in a.u.).

The dipole–dipole many-body interaction potential, i.e., including many-body dispersion, is

$$U = U_{\mathrm{LJ}} + U_{\mathrm{disp}} \tag{3}$$

with the many-body dispersion energy[2]

$$U_{\mathrm{disp}} = -\left(1 - \frac{\alpha_{\mathrm{eff}}^2}{\alpha^2}\right) U_{\mathrm{LJ}} \tag{4}$$

It is assumed that only the atomic dipole polarization charges, i.e., the atomic dipolar polarizability α, contributes to the dispersion interaction. With regard to the results this approximation seems to be sufficient to resolve relative stabilities and magic numbers of $^4\mathrm{He}_{4-13}$ clusters.

As in the previous paper,[2] the dipole–dipole many-body long-range interaction part enters via the effective polarizability of the polarization model

$$\alpha_{\mathrm{eff}} = \frac{1}{3n} \mathbf{Tr} \langle \alpha(\mathbf{1} - \alpha\mathbf{G})^{-1} \rangle \tag{5}$$

Essentially α_{eff} is the trace of the Metropolis Monte Carlo averaged ($\langle \cdots \rangle$) inverted $3n \times 3n$ dipole propagator $\mathbf{G}$ with matrix elements

$$G_{ij}^{st} = -\frac{1}{|r_{ij}^{st}|^3}\left(1 - 3\,\frac{r_i^s r_j^t}{|r_{ij}^{st}|^2}\right) \tag{6}$$

where s, t are the coordinate indices and i, j the atom indices, respectively. Note that the n-body interaction is calculated before averaging. Thus, α_{eff} is the mean value calculated with the exact n-body dipole interaction, and not calculated with a mean (dipole) field $[1/3n)]\,\mathbf{Tr} < \alpha(\mathbf{1} - \alpha\mathbf{G})\rangle^{-1}$.

RESULTS AND DISCUSSION

The classical, the PIMC, and the all order many-body simulations of clusters were carried out at fixed temperature of 3.2 K and run over some 10^4 iterations. The resulting spectrum of binding energies for $^4\mathrm{He}_n$ is compared with the mass spectrum by Stephens and King,[5] i.e., the measured relative frequency of $^4\mathrm{He}_n$ clusters.

Figure 1 shows the binding energies of $^4\mathrm{He}_n$ clusters calculated with the classical Monte Carlo simulation of helium atoms and the LJ(12, 6) potential. Assuming that high cluster binding energies are responsible for the occurrence of magic numbers in cluster beam mass spectroscopy, the classical simulation of $^4\mathrm{He}_{4-13}$ shows magic numbers for $^4\mathrm{He}_8$ and $^4\mathrm{He}_{10}$, which do not correspond to the measured magic numbers 7 and 10.[5]
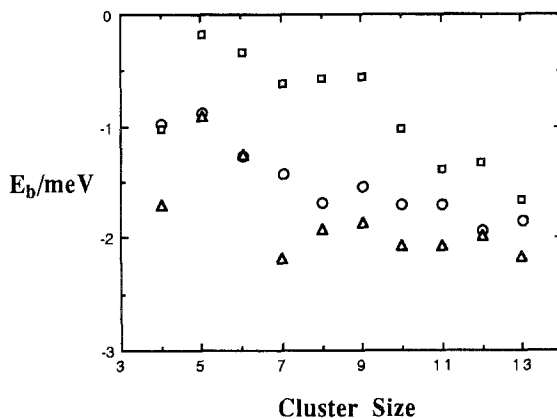

Fig. 1. Binding energies of $^4\mathrm{He}_n$ clusters at 3.2 K calculated with ($\bigcirc$) classical Monte Carlo simulation, ($\square$) PIMC, i.e., treating helium atoms as quantum statistical point particles, and ($\triangle$) with the all-order n-body (n is the cluster size) Monte Carlo simulation in the dipole dispersion approximation including short-range corrections, i.e., the helium atoms are considered as polarizable point particles with quantum mechanical dipolar n-body dispersion interaction.

The semiclassical simulation of ^4He_n with PIMC and the LJ(12, 6) potential is used with an optimized number of virtual time steps. Among some runs with different numbers of virtual time steps with up to 1025 steps, it was found that a simulation with 257 virtual time steps minimizes the variances of both the potential and the kinetic energy. The calculated high binding energy for $^4He_7$ and the relative binding energies up to $^4He_9$ correlate with the mass spectrum by ref. 5, but for greater ^4He_n clusters PIMC failed, too.

With the same number of iterations the semiclassical simulation of $^4He_{4-13}$ clusters in the polarization model, i.e., with a many-body dispersion interaction, shows good agreement of binding energies with the ^4He_n mass spectrum by Stephens and King.[5] In particular, the magic numbers 7 and 10 and the relative unstability of $^4He_9$ and $^4He_{12}$ could be resolved.

CONCLUSION

In conclusion, $^4He_{4-13}$ clusters have been simulated at 3.2 K with classical Monte Carlo, with path integral Monte Carlo (PIMC), and with the all order many-body Monte Carlo procedures (polarization model).[2] The calculated $^4He_{4-13}$ binding energies obtained from simulations were compared to the TOF experiments by Stephens and King,[5] assuming that the cluster binding energies correlate with the cluster-size frequency in cluster beam TOF experiments. With classical Monte Carlo and PIMC the helium atoms could interact via the two-body Lennard-Jones (12, 6) potential. In the all-order many-body Monte Carlo regime the Lennard-Jones potential has been modified by a static dipole dispersion interaction term that is calculated from the n-body (n is the cluster size) dipole propagator. The classical simulation with LJ(12, 6) failed in describing certain stabilities of ^4He_n clusters, for the Lennard-Jones potential does not include any quantum corrections known to be important for atomic systems with low-mass atoms and systems with low temperature. Although the binding energies calculated with the path integral Monte Carlo model, i.e., treating the helium atoms as quantum statistical point particles, have shown structure which correlates more with the TOF experiment, the model was unable to resolve details of the spectrum. Only the all-order many-body simulation within the polarization model regime in the dipole approximation with short-range corrections resolved the characteristic structures of the TOF mass spectrum. From the results presented here, we conclude that the stabilization of ^4He_n clusters seems to be more affected by long-range many-body processes (which are quantum mechanical in origin) than by quantum statistical motion of their atoms simulated with PIMC. Further investigations on ^3He_n and ^4He_n clusters which in addition include spin

statistics will show whether collective long-range interactions have more influence on the stability of helium clusters than the quantum statistics of their atoms. Also, it might be interesting to see the cluster size for which quantum statistical correlations become important.

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