Monte-Carlo studies of bosonic van der Waals clusters.

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In a previous paper [1], we developed a form of variational trial wave function and applied it to van der Waals clusters: five or less atoms of Ar and Ne modeled by the Lennard-Jones potential. In addition, we tested the trial functions for a hypothetical, light atom resembling Ne but with only half its mass. We did not study atoms such as He\(^4\) with larger de Boer parameters, i.e., systems in which the zero point energy plays a more important role relative to the potential energy. This is the main purpose of the present paper. In fact, we study clusters to the very limit where the zero-point energy destroys the ground state as a bound state. A simple picture of this un-binding transition predicts the power law with which the energy vanishes as the de Boer parameter approaches its critical value and the power of the divergence of the the size of the clusters in this limit. Our numerical results are in agreement with these predictions.

I. INTRODUCTION

We consider clusters of bosonic Lennard-Jones atoms for which we present two sets of results. Firstly, there are improved estimates of the ground state energies of systems studied previously with variational Monte Carlo [1]. The improvements were obtained with a modified diffusion Monte Carlo algorithm [2], similar to Ref. [3]. Secondly, we study the behavior of the clusters for small masses. That is, in reduced units such that the Lennard-Jones pair potential has the form \(r^{-12} - 2r^{-6}\), the only independent parameter in the Schrödinger equation is the reduced inverse mass \(m^{-1}\), a quantity proportional to the square of the de Boer parameter. As the de Boer parameter increases, the relative importance of the zero-point energy and the ground state energy of a cluster increase, as does its size. At a critical value of the de Boer parameter the ground state energy \(E_0\) vanishes while average cluster size \(\langle r \rangle\), as defined below, diverges and the cluster ceases to exist in a bound state.

For the simple case of a dimer one can show that

\[
\begin{align*}
E_0 |_{m \downarrow m_c} & \sim \Delta m^2, \\
\langle r \rangle |_{m \downarrow m_c} & \sim \Delta m^{-1}.
\end{align*}
\]

where \(\Delta m = m - m_c\) with \(m_c\) the critical value of the reduced mass. Note that \(m_c\) depends on \(N\), the number of atoms in the cluster and is expected to be a monotonically decreasing function of \(N\). The mathematical mechanism that yields Eqs. (1) is the following. Two scattering states forming a complex conjugate pair merge at zero momentum to produce two states with “complex momentum”: a physically acceptable bound state and a state with unacceptable behavior at infinity. This mechanism is probably not limited to the dimer and it is quite plausible that Eqs. (1) apply in general to clusters of any finite size.

II. RESULTS

Table [1] shows the comparison between the ground state energy estimates obtained by using variational Monte Carlo [1] and our improved diffusion Monte Carlo algorithm. Results obtained by variational Monte Carlo suffer from a systematic bias, i.e., if we denote by \(E_T = \langle \psi_T | \mathcal{H} | \psi_T \rangle\), the variational estimate obtained a given normalized trial state \(| \psi_T \rangle\), one has \(E_0 < E_T\), where the equality holds only if the trial function is the exact ground state wave function.

If one defines

\[
\chi^2 = \langle \psi_T | (\mathcal{H} - E_0)^2 | \psi_T \rangle
\]

the following inequality holds (see Ref. [1] for details and references):

\[
0 < E_T - E_0 < \frac{\chi^2}{E_1 - E_0},
\]
TABLE I. Estimates of the ground state energies $E_0$ for noble gases Ar and Ne and hypothetical lighter particle $^\frac{1}{2}$-Ne obtained by using improved diffusion algorithm compared with estimates $E_T$ taken from Ref. [1]. Standard errors in the last digit are given in parentheses. Estimates of the relative errors, as described in text, are given by $Q'$ and $Q''$. Missing values indicate cases where the statistical errors are smaller than the errors due to numerical differentiation.

| $N$ | Ar  | Ne   | $^\frac{1}{2}$-Ne |
|-----|-----|------|-------------------|
| 3   | -2.553335364(1) | -1.7195589(3) | -1.308443(2) |
|     | -2.553335375(2) | -1.7195586(5) | -1.308444(1) |
| 4   | -5.1182368(2)   | -3.464174(8)  | -2.64356(3)   |
|     | -5.1182376(4)   | -3.464229(13) | -2.64383(4)   |
| 5   | -7.78598(1)     | -5.29948(8)   | -4.0669(1)    |
|     | -7.7862(5)      | -5.3037(3)    | -4.0748(5)    |

where $E'_1$ is the energy of the first, totally symmetric excited state. To estimate the number of correct digits in the variational estimate of the ground state and to ascertain how good a bound inequality (3) is we introduce the following quantities:

\[
Q' = -\log_{10} \left( \frac{\chi^2}{(E'_1 - E_T)|E_T|} \right),
\]

\[
Q'' = \frac{\chi^2}{(E'_1 - E_T)(E_T - E_0)}.
\]

The results are shown in Table I. Quite remarkably, the bound given in Eq. (3) is very tight.

Next we compare the behavior of the ground state energy on mass with the behavior predicted by Eqs. (1). Fig. 1 shows the energy as a function of the de Boer parameter for clusters of sizes $N = 3, 4$ and 5. The energy has been normalized by dividing by the classical ground state energy and we note that the linear behavior for small de Boer parameter, i.e., large mass, follows from the harmonic approximation. Fig. 2 explicitly shows the data in a double-logarithmic plot of the ground state energy vs the deviations from the respective critical points.

The average size of the clusters was expressed in terms of $r_{ij}$, the distance between atoms $i$ and $j$, using the following two definitions: (1) $r = 2(r_{ij})/N(N - 1)$ (2) $R = (2(r_{ij}^2)/N(N - 1))^{1/2}$. Double logarithmic plots of the
average size vs the deviations from the respective critical points are shown in Figs. 3 and 4. It should be noted that in contrast to the diffusion Monte Carlo estimates of the energy, the estimates of the average size are biased in the sense that for any operator $A$ that does not commute with the Hamiltonian diffusion Monte Carlo yields the matrix element $\langle \psi_T | A | \psi_0 \rangle$ rather than the ground state expectation value $\langle \psi_0 | A | \psi_0 \rangle$. The values shown in the figures were obtained by linear extrapolation from $\langle \psi_T | A | \psi_T \rangle$ and $\langle \psi_T | A | \psi_0 \rangle$. Irregularities in the quality of the trial functions are presumably responsible for the corresponding irregularities in the average cluster sizes for the smallest masses in the $N = 5$ case.

III. CONCLUSIONS

We presented estimates of the ground state energies of van der Waals clusters in a wide range of masses. The results show that wave functions introduced in Ref. [1] provide good trial function in the whole range from the classical limit to the ultra-quantum limit, where the clusters cease to form a bound state. Results for the behavior in the vicinity of the un-binding transition corroborate Eqs. (eq.critical). The agreement for the case of the energy is very good; for the divergence in the size dependence the average cluster size of the clusters closest to the transition was not quite large enough to show the asymptotic “critical behavior.”

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[1] A. Mushinski and M.P. Nightingale, J. Chem. Phys. 101, 8831 (1994).
[2] M. Meierovich, A. Mushinski and M.P. Nightingale, (unpublished).
[3] C.J. Umrigar, M.P. Nightingale and K.J. Runge, J. Chem. Phys. 99, 2865 (1993).
FIG. 3. Log-log plot of the average cluster size \( r \) as defined in the text vs. the deviation from the un-binding transition, \( m - m_c \).

FIG. 4. Log-log plot of the gyration radius \( R \) vs. the deviation from the un-binding transition, \( m - m_c \).