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Transitioning Model Potentials to Real Systems. II. Application to Molecular Oxygen

by Scott D. Bembenek and Betsy M. Rice

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Abstract

Recently, we introduced a novel computer simulation technique to determine the optimal set of parameters of an interaction potential for a simple monatomic liquid. This technique was used to obtain interaction potentials of the Lennard-Jones form that accurately describe argon over its entire liquid phase at a fixed pressure (S. D. Bembenek and B. M. Rice, Mol. Phys. 97, 1085 [1999]). Here, we extend this technique to a homonuclear diatomic molecular system, liquid oxygen. This technique was first applied to a system in which the oxygen molecules were treated as point masses interacting through a modified Lennard-Jones potential. Simulations using the resulting optimal set of potential parameters of this system predict densities that are within 0.25% of experiment over the entire liquid range of oxygen at a fixed pressure. However, the errors in the internal energy and the enthalpy were as large as 9.8%. The technique was then used to determine the optimal parameters for a system of harmonic molecules, in which each molecule has two interaction sites centered at the atomic nuclei. The intermolecular interaction is the sum of all site-site interactions described by a modified Lennard-Jones potential. Simulations using these parameters reproduce experimental densities with an error no greater than 0.80%. The predictions of the internal energy and enthalpy differ from experiment by no more than 3.0% for temperatures below 90 K; predictions at 90 K differ from experiment by no more than 4.11%. These results seem to suggest that our method for determining parameters for an interaction potential is also applicable to simple molecular systems.

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Transitioning model potentials to real systems. II. Application to molecular oxygen

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Recently, we introduced a novel computer simulation technique to determine the optimal set of parameters of an interaction potential for a simple monatomic liquid. This technique was used to obtain interaction potentials of the Lennard-Jones form that accurately describe argon over its entire liquid phase at a fixed pressure [S. D. Bembenek and B. M. Rice, Mol. Phys. **97**, 1085 (1999)]. Here, we extend this technique to a homonuclear diatomic molecular system, liquid oxygen. This technique was first applied to a system in which the oxygen molecules were treated as point masses interacting through a modified Lennard-Jones potential. Simulations using the resulting optimal set of potential parameters of this system predict densities that are within 0.25% of experiment over the entire liquid range of oxygen at a fixed pressure. However, the errors in the internal energy and the enthalpy were as large as 9.8%. The technique was then used to determine the optimal parameters for a system of harmonic molecules, in which each molecule has two interaction sites centered at the atomic nuclei. The intermolecular interaction is the sum of all site–site interactions described by a modified Lennard-Jones potential. Simulations using these parameters reproduce experimental densities with an error no greater than 0.80%. The predictions of the internal energy and enthalpy differ from experiment by no more than 3.0% for temperatures below 90 K; predictions at 90 K differ from experiment by no more than 4.11%. These results seem to suggest that our method for determining parameters for an interaction potential is also applicable to simple molecular systems.

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I. INTRODUCTION

Computer simulations are routinely used to complement experimental studies of physical systems. They allow for the assessment of physical models that are used in the interpretation of experimental information. They can also be used to investigate the system at conditions that might be difficult to probe through experiment. Central to the success of a simulation is the interaction potential. The accurate predictions of thermodynamic and transport properties depend on a ''good'' interaction potential, one that correctly describes the fundamental properties of the system. Arriving at an interaction potential that accurately models the desired system can be a cumbersome task. Often, an interaction potential that is parametrized to reproduce properties at a single phase point for the system does not adequately predict the same properties at different phase points. In such a case, the model is of limited use. Therefore, it is desirable to have an interaction potential that will predict the properties of a system over a wide range of phase space. Common approaches to developing such interaction potentials involve the inclusion of extremely complex functions or a large number of terms. Interaction potentials with a complicated form can be time consuming to use in computer simulations and difficult, if not impossible, to use in analytical calculations. Therefore, the ideal interaction potential will reproduce the relevant physical and chemical behavior of the system over a wide range of phase space and will also be mathematically simple enough to allow for ease of computation.

Recently, we have introduced a method to optimize an interaction potential.[1] It was shown that a Lennard-Jones-like interaction potential with the set of parameters optimized by the approach described herein accurately describes the thermodynamic properties of argon over its whole liquid phase at several pressures. This set of potential parameters was obtained with a novel application of classical molecular simulations, whereby parameters of the interaction potential are continuously adjusted during isothermal–isobaric (NPT) simulations such that the experimental bulk density is reproduced. We demonstrated this approach using both NPT molecular dynamics (MD) and Monte Carlo (MC) simulations. For the molecular dynamics simulations, we assumed that the system of argon atoms interacted through a modified Lennard-Jones potential,

$$v(r)=4\epsilon\left[\left(\frac{\sigma}{r}\right)^{12}-\left(\frac{\sigma}{r}\right)^{6}\right]+Ar^2+B, \tag{1.1}$$

where A and B are constant and chosen such that both the potential and the force are continuous at the potential cutoff, r_{cut}. A standard Lennard-Jones interaction potential was

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used in the demonstration of the method using NPT-MC simulations, with long-range corrections included to account for all interactions between pairs of atoms whose distances exceeded r_{cut}.

During optimization of the potential parameters, the system was constrained to obtain the experimental densities over the entire temperature range for the liquid phase of argon at a single pressure. For each temperature investigated, a series of simulations was performed with different values of σ. For a given simulation in which the temperature, pressure, and σ value were fixed, the bulk density constraint was imposed by allowing ϵ to vary according to

$$\epsilon(t)=\epsilon_0+\lambda\sum_{t'=1}^{t}\Delta\rho(t'), \tag{1.2}$$

for the MD simulations and

$$\epsilon_{\mathrm{step}}=\epsilon_0+\lambda\sum_{i=1}^{\mathrm{step}}\Delta\rho_i, \tag{1.3}$$

for the MC simulations. In these equations, λ is the coupling strength, ϵ_0 is an initial value for ϵ, and $\Delta\rho$ is the difference between the desired and instantaneous bulk density at each step in the simulation. If the system is too dilute, i.e., the instantaneous bulk density is less than the desired bulk density, ϵ will be made larger. Similarly, if the system is too dense, then ϵ will be made smaller. At the initial portions of the parametrization trajectories, the values of ϵ will vary dramatically in time as the system attempts to achieve the experimental bulk density. The corresponding instantaneous densities during this portion will show large fluctuations about the experimental bulk density. At later portions of these trajectories, the density fluctuations will become smaller as will the fluctuations in ϵ. At this point, the value of ϵ can be chosen. This procedure is done over a range of σ's for a given temperature and several trajectories are used to obtain an average value of ϵ, $\langle\epsilon\rangle$ for each σ. Obtaining $\langle\epsilon\rangle$ over a range of temperatures will result in one set of σ and $\langle\epsilon\rangle$ that will recur at each temperature (within statistical error); this is called the "common set" of parameters. Since the form of interaction potential in the MD runs [Eq. (1.1)] was different than that used in the MC runs (a standard Lennard-Jones), as one would expect,[2] the resulting parameter sets were different.

In the previous work, we showed that MD simulations using the common set reproduced the bulk densities, internal energies, and enthalpies of argon over its entire liquid phase at 40 bar to within 1% of experimental values. The self-diffusion coefficients for argon determined using this model were within 8% of experimental values. We also showed that MC simulations using the common set reproduced the bulk densities, internal energies, and enthalpies for argon over the liquid phase at 40 bar to within 6% of experimental values. Molar volumes predicted for liquid argon at temperatures ranging from 100–140 K and pressures ranging from 100–600 atm were found to be within 1% of experimental values.

In this work, we implement this same technique to obtain modified Lennard-Jones potentials for two model systems of liquid oxygen. Reasonable interaction potentials for molecular oxygen exist;[3,4] however, we have chosen the oxygen system to demonstrate the applicability of this method to a simple molecular system. Our first model, denoted "model 1," treats diatomic oxygen as a single particle, thus excluding rotational and vibrational degrees of freedom. As we will discuss further in Sec. III, simulations using this model do not generate internal energies and enthalpies that are in good agreement with experiment (although the bulk densities are in excellent agreement). In an effort to improve the overall performance, we then treat each molecule as a pair of atoms interacting through a simple harmonic potential. The intermolecular interaction between a pair of molecules is the sum of all atom–atom interactions. This model is denoted as "model 2." The atom–atom interactions are described by the modified Lennard-Jones potential in Eq. (1.1). The parameters for the intermolecular interaction potential are determined in the same manner as described above.

Calculation details are described in Sec. II. Results and discussion will be given in Sec. III with conclusions drawn in Sec. IV.

II. DETAILS OF THE CALCULATIONS

A. Model 1: Diatomic particles

The system consisted of 500 "diatomic particles" interacting through a modified Lennard-Jones potential [Eq. (1.1)]. The potential parameters were determined using NPT-MD simulations in a manner similar to that for liquid argon and briefly described in Sec. I. A detailed description of the methodology has been given in our earlier study.[1] The cutoff for the interaction potential, r_{cut}, is 3.50 σ. In our previous study with liquid argon,[1] we illustrated the dependence of the parameter set $\{\epsilon, \sigma\}$ on the r_{cut}. The value of ϵ continually decreased with increasing r_{cut} while the value of σ remained unchanged at 3.40 Å, up to $r_{\mathrm{cut}}=6.00\ \sigma$. The behavior of ϵ with increasing r_{cut} suggested that the parameter set would converge to a single set of values with increasing r_{cut} for the form of potential described by Eq. (1.1). However, it was also noted that the parameter sets determined using $r_{\mathrm{cut}}\geqslant 3.50\ \sigma$ gave very good results for energy, enthalpy, and density as well. Since it is always desirable to minimize CPU cycles while still obtaining accurate results, we have chosen $r_{\mathrm{cut}}=3.50\ \sigma$.

Particle masses were set to 31.9988 amu and all simulations, except otherwise stated, were run at a pressure of 1 bar. The pressure was held constant using Andersen's method,[5] making it necessary to choose a piston mass. A larger mass will result in better momentum conservation than a smaller one, but the system will explore volume space more slowly. In an effort to satisfactorily conserve momentum and sample volume space in a reasonable amount of time, the mass was chosen to be $1\cdot 10^{-3}$ amu Å^{-4}. Finally, the temperature was held constant through a simple scaling of velocities and the equations of motion were integrated, with a time step of 5.1 fs, using a modified velocity-Verlet algorithm,[2,6] which eliminated the need for scaled coordinates.[7,8] Periodic boundary conditions were applied in all directions.

Initially, velocities and accelerations were set to zero

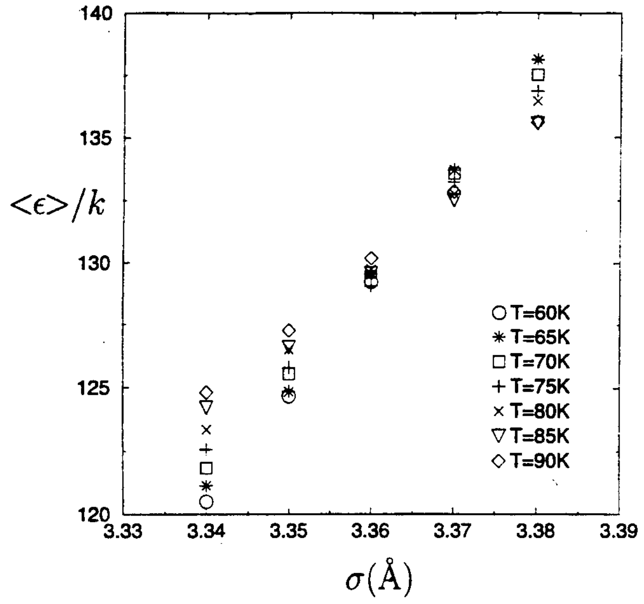

FIG. 1. The value of $\langle \epsilon \rangle /k$ and the corresponding σ for liquid oxygen (as a diatomic particle) at a pressure of 1 bar is shown for several temperatures. The common set $\{\epsilon, \sigma\}$ occurs at {129.564 K, 3.36 Å}.

and the particles were randomly displaced a small amount from a face-centered-cubic (fcc) lattice. Then, an NVT-MD simulation consisting of 100 000 steps was performed at 90 K, which is in proximity to the normal boiling point.[9] The ending coordinates of this trajectory were then used as starting coordinates for all parametrization runs. NPT-MD simulations were used for the determination of the potential parameters.

Figure 1 shows the average value of ϵ (scaled by Boltzmann's constant, k) versus σ for liquid oxygen (as a diatomic particle) at temperatures over the range 60–90 K. The average value of ϵ for each σ is the result of five runs with at least 25 000 time steps in a given run. The σ value of the common set corresponds to the point at which the range of the temperature-dependent ϵ values is a minimum. The ϵ value of the common set is the average of the temperature-dependent ϵ values at this point. The location of the σ value of the common set is very apparent in this figure; it is located at 3.36 Å. The ϵ of the common set is 129.564 K.

These potential parameters were then used in production runs to obtain values for density, internal energy, and enthalpy over the whole liquid range. Initial conditions for these trajectories were generated in the same fashion as those generated for the parametrization runs, except that the common set was used. Each trajectory consisted of 110 000 time steps. The first 10 000 time steps allowed for equilibration and the remaining 100 000 time steps were used to calculate averages. Averages were calculated for temperatures ranging from 55–90 K, in intervals of 5 K.

B. Model 2: Harmonic molecules

Although the diatomic particle system was able to reproduce experimental densities very well, its ability to reproduce experimental internal energies and enthalpies was unsatisfactory, as will be discussed more fully in the next section. Consequently, we enhanced the model system to allow for molecular shape and intramolecular vibration. In this model, each oxygen molecule was represented as a pair of atoms, with a harmonic intramolecular interaction and an intermolecular site–site interaction[6] (with sites located at the atomic nuclei) described by the modified Lennard-Jones potential. This enhancement allowed for the incorporation of rotational and vibrational degrees of freedom in the simulations.

The system consisted of 250 diatomic molecules. The mass of each oxygen atom was set to 15.9994 amu. The atoms within the same molecule interacted through a harmonic potential with an equilibrium distance of 1.208 Å and a force constant of 73.556 39 eV Å^{-2}.[10,11] Intermolecular site–site interactions were via Eq. (1.1) with a potential cutoff, $r_{\mathrm{cut}} = 3.50\ \sigma$. The temperature was held constant by scaling the center-of-mass velocities and the pressure was held constant using Andersen's method.[5] The piston mass was chosen to be $5 \cdot 10^{-4}$ amu Å^{-4} and the time step was decreased to 1.02 fs. The molecules were initialized to a body-centered-cubic (bcc) lattice with the center of mass being placed at the lattice site. For each molecule, a vector with length equal to the equilibrium bond distance was used. The direction of the vector was randomly generated and was placed such that its center was located at a lattice site. One of the atoms in the given molecule was located at one end of the vector and the other atom was placed at the opposite end of the vector. Particle velocities and accelerations were set to zero and an NVE-MD simulation was performed for 10 000 time steps. The trajectory was stopped and the final coordinates were used for an NVT-MD simulation of the system at 90 K. The trajectory was integrated for 100 000 time steps. These ending coordinates were then used as starting coordinates for the parametrization runs.

The same technique for finding the common set (as discussed in Sec. I and elsewhere[1] in detail) was used. Figure 2 shows ϵ (scaled by Boltzmann's constant) versus σ for all temperatures studied. Here, the value of ϵ is the result of at least 100 000 time steps for each σ. This is slightly different from the diatomic particle case, where ϵ was obtained as an average of five runs, each consisting of at least 25 000 time steps for each value of σ.

Unlike the diatomic particle case, the set of recurring parameters is not as obvious as in Fig. 2. However, aside from 90 K, the points at $\sigma = 3.010$ Å are in good proximity to each other and correspond to the point at which the range of the temperature-dependent ϵ is a minimum. Most likely, the point at 90 K is reflecting the proximity of the system to the boiling point.[9] This same effect was seen, to a lesser extent, in our previous study.[1] The ϵ in the common set was obtained by excluding the point at 90 K and averaging over the remaining points. The resulting value for ϵ is 55.128 K.

In order to assess the quality of the interaction potential, NPT-MD simulations using Eq. (1.1) and parameters of the common set were used to generate thermodynamic properties of oxygen over its entire liquid phase at 1 bar. Initial conditions were generated in the same manner as for those used in the parametrization runs, except that the common set of parameters was used. Each trajectory consisted of 250 000 time

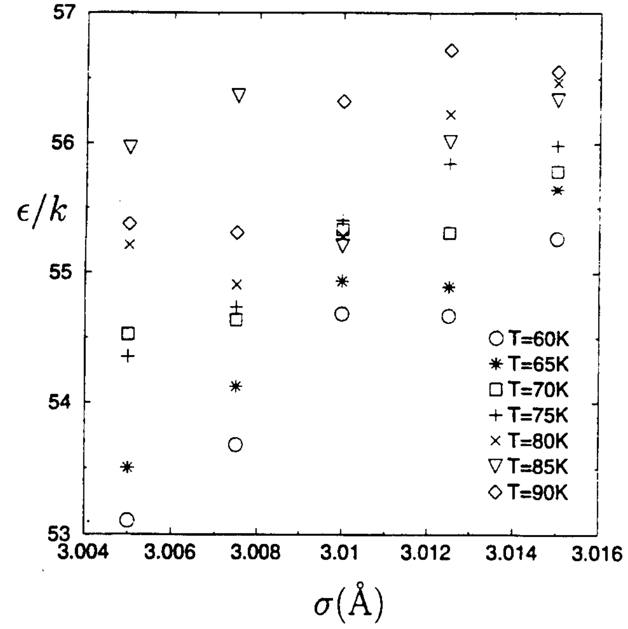

FIG. 2. The value of ϵ/k and the corresponding σ for liquid oxygen (as a harmonic molecule) at a pressure of 1 bar is shown for several temperatures. The common set $\{\epsilon, \sigma\}$ occurs at {55.128 K, 3.010 Å}.

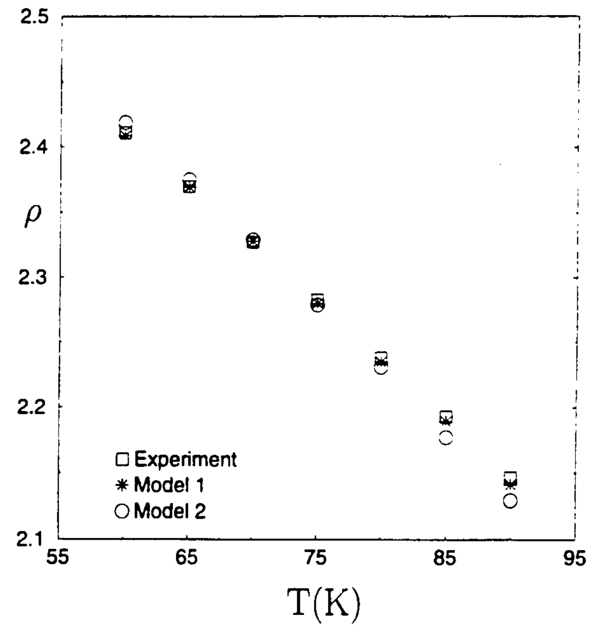

FIG. 3. The number density (molecules Å^{-3}) as a function of temperature is shown for molecular dynamics simulations of liquid oxygen as a diatomic particle (model 1) and as a harmonic molecule (model 2) using the common set of potential parameters found in this work. The experimental values (Ref. 9) are also shown. The error bars have been eliminated since they are comparable to the size of the symbols. The density has been multiplied by 10^2 for convenience.

steps at the desired temperature with the initial 50 000 time steps used for equilibration. The initial 50 000 time steps were more than enough for the system to exhibit the Boltzmann distributions for the translational, rotational, and vibrational components, as well as to obtain the expected averages of 3/2 kT and kT for the translational and rotational kinetic energies, respectively. The final 200 000 time steps were used to calculate averages.

III. RESULTS AND DISCUSSION

A. Model 1: Diatomic particles

Predicted densities, internal energies, and enthalpies for this model are shown in Figs. 3–5 for all temperatures except 55 K, along with the experimental data[9] and the results for the molecular system (model 2). These data are also presented in Table I.

The error in density is no greater than 0.25% over the whole temperature range, but the deviations from experiment for the internal energies and enthalpies are as large as 9.8%. This difference was not observed in the application of the method for argon,[1] where the agreement between the predicted and experimental internal energies was excellent. The internal energies predicted by model 1 are too low by at least 1/2 kT, which suggests to us that the diatomic particle approximation is inadequate.

At 55 K this system undergoes a phase transition to a solid, thereby making it impossible to obtain ensemble averages for this phase point. To make a qualitative comparison to the normal melting point, the system was heated to 90 K at a pressure of 1 atm and the simulation allowed to proceed for 100 000 time steps. Then it was instantly cooled to 55 K and the equations of motion were integrated for another 100 000 time steps. Figure 6 shows the radial distribution function [as $g(r^2)$] after this final run. From this, one sees that the system has solidified. The radial distribution function is clearly showing a disordered solid—a glass, in this case. If the system were truly at the crystal (global) minimum, then further relaxation would, in theory, produce the ordered solid. How-

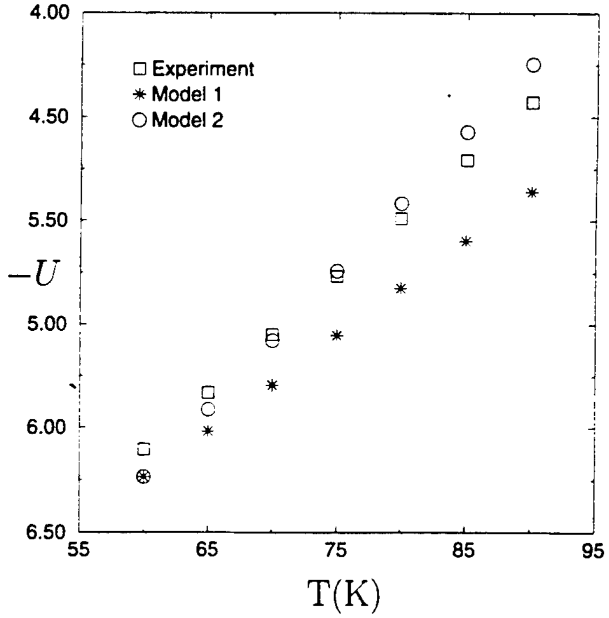

FIG. 4. The internal energy (eV molecule^{-1}) as a function of temperature is shown for molecular dynamics simulations of liquid oxygen as a diatomic particle (model 1) and as a harmonic molecule (model 2) using the common set of potential parameters found in this work. The experimental values (Ref. 9) are also shown. The error bars have been eliminated since they are comparable to the size of the symbols. The energy has been multiplied by 10^2 for convenience.

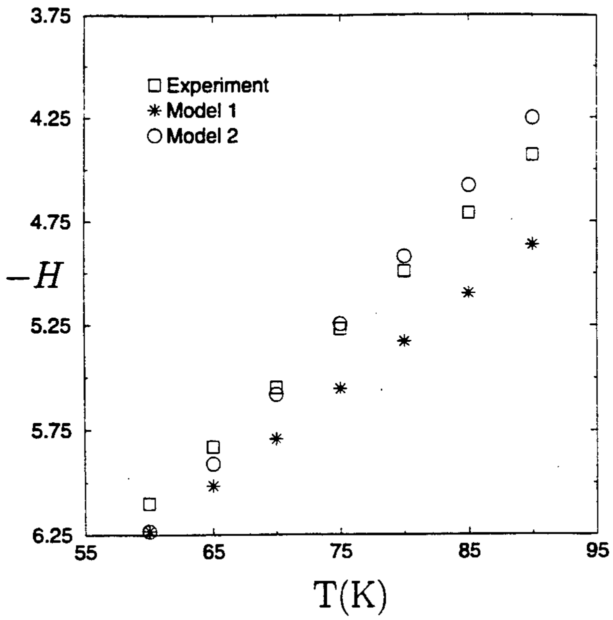

FIG. 5. The enthalpy (eV molecule^{-1}) as a function of temperature is shown for molecular dynamics simulations of liquid oxygen as a diatomic particle (model 1) and as a harmonic molecule (model 2) using the common set of potential parameters found in this work. The experimental values (Ref. 9) are also shown. The error bars have been eliminated since they are comparable to the size of the symbols. The enthalpy has been multiplied by 10^2 for convenience.

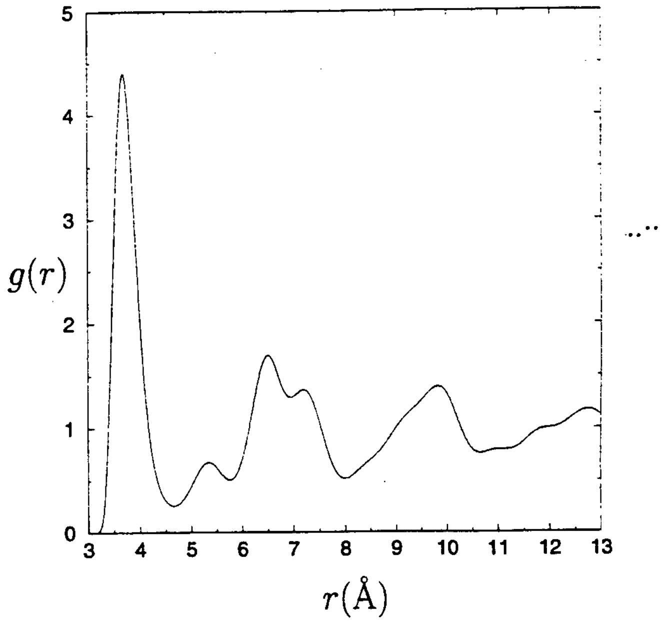

FIG. 6. The radial distribution function [as $g(r^2)$] for liquid oxygen (as diatomic particles) from a molecular dynamics simulation at 55 K and 1 atm.

ever, if it was cooled too quickly, the system will have missed the crystal minimum and thereafter, be supercooled until solidification occurs at some lower temperature; a faster cooling rate will cause this transition temperature to be higher. Nonetheless, since the cooling rate for the system was instantaneous, the observed transition should provide a lower bound to the melting temperature. That is to say, the melting point of the system cannot occur at a lower temperature.

B. Model 2: Harmonic molecule

Densities, internal energies, and enthalpies using this model are shown in Figs. 3–5 for all temperatures studied along with the experimental data[9] and the results for the diatomic particle system (model 1). These data are also presented in Table I. The error in density is no greater than 0.80% over the temperature range studied, while the values of internal energy and enthalpy deviate from experimental values by no more than 4.11%. The largest error occurs at 90 K. This is easily understood since this point was excluded from the average value of ϵ as mentioned earlier. For all temperatures below 90 K, the predicted internal energies and enthalpies are within 3% of the experimental values. The addition of the molecular degrees of freedom to this model clearly provides a substantial improvement over the diatomic particle model.

As seen in the last section, the diatomic particle model did very well at obtaining the densities but was approximately in error $kT/2$ for the energies and enthalpies. The improvement offered by the harmonic molecule makes it clear that some of the disagreement between the results of model 1 and experiment is due to the exclusion of the rotational and vibrational degrees of freedom. One might then expect an error of kT plus another $kT/2$ attributed to the rotational and vibrational contributions, respectively. However, the larger value of ϵ required by the diatomic particle system to obtain the density may partially compensate for the

TABLE I. Density, internal energy, and enthalpy for liquid oxygen.

	ρ (molecules/Å^3)$\cdot 10^2$			$-U$ (eV/molecule)$\cdot 10^2$			$-H$ (eV/molecule)$\cdot 10^2$		
T (K)	Expt. (Ref. 9)	Model 1	Model 2	Expt. (Ref. 9)	Model 1	Model 2	Expt. (Ref. 9)	Model 1	Model 2
60	2.4112	2.4089	2.4189	6.1037	6.2346	6.2354	6.1010	6.2320	6.2341
65	2.3693	2.3690	2.3749	5.8316	6.0179	5.9120	5.8290	6.0153	5.9107
70	2.3262	2.3271	2.3281	5.5498	5.7941	5.5802	5.5471	5.7914	5.5789
75	2.2824	2.2801	2.2786	5.2679	5.5548	5.2430	5.2652	5.5521	5.2416
80	2.2380	2.2348	2.2308	4.9893	5.3252	4.9170	4.9865	5.3224	4.9156
85	2.1927	2.1893	2.1772	4.7074	5.0967	4.5717	4.7046	5.0939	4.5702
90	2.1464	2.1410	2.1292	4.4289	4.8609	4.2470	4.4260	4.8580	4.2485

absence of vibrational and rotational motions. This could explain why the system does not miss the full 3/2 kT but rather only $kT/2$.

IV. CONCLUSIONS

Interaction potentials of the Lennard-Jones form for two model systems of liquid oxygen were obtained through a novel application of classical molecular dynamics. The interaction parameters $\{\epsilon, \sigma\}$ for both models were obtained in a similar manner to that previously described for liquid argon.[1] In this approach, parameters of the interaction potential are continuously adjusted during isothermal–isobaric simulations (NPT-MD or NPT-MC) such that the experimental density of the system is achieved. Application of this procedure over a given temperature range results in an optimized set of parameters called the common set.

In the first model, diatomic oxygen was described as a single particle; thus, rotational and vibrational degrees of freedom were not treated. NPT-MD simulations using this simple model predicted densities that were within 0.25% of experiment over the entire temperature range of the liquid phase (for a pressure of 1 bar). Unfortunately, the deviations of the internal energies and the enthalpies from experiment were as large as 9.8%.

An NPT-MD simulation of the system was also performed at the normal melting point of 55 K. The resulting radial distribution function [as $g(r^2)$] showed that the system solidified into a glass. Since the cooling rate of the system was instantaneous, this should provide a lower bound to the melting point for this model.

In an effort to improve the agreement of predictions of internal energies and enthalpies with experiment, we refined our model of molecular oxygen by treating each molecule as a pair of atoms interacting through a harmonic interaction potential. The intermolecular site–site interactions[6] (with sites located at the atomic nuclei) were via a modified Lennard-Jones potential, with potential parameters $\{\epsilon, \sigma\}$ of {55.128 K, 3.010 Å}, respectively. This system offered a significant improvement over the diatomic particle model. Predictions of densities differed from experiment by no more than 0.80%. The predictions of internal energies and enthalpies differed from experiment by no more than 3.0% for temperatures less than 90 K; predictions at 90 K differed from experiment by no more than 4.11%.

Although not explored here, our previous results[1] indicate that one might expect to do well at pressures other than the one used to optimize the interaction potential, which would allow access to state points outside the original range. Overall, the method has been easy to implement and able to yield accurate Lennard-Jones-like potentials. Clearly, the method is generalizable to other potential forms. The simple systems studied thus far also suggest that the method is generalizable to other systems as well. If this is indeed the case, it may prove the bulk density to be an optimal constraint in determining the microscopic interactions of the system.

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[1] S. D. Bembenek and B. M. Rice, Mol. Phys. **97**, 1085 (1999).
[2] D. Frenkel and B. Smit, *Understanding Molecular Simulations* (Academic, London, 1996).
[3] B. Saager and J. Fischer, Fluid Phase Equilibria **66**, 103 (1991).
[4] Y. Miyano, Fluid Phase Equilibra **104**, 71 (1995).
[5] H. C. Andersen, J. Chem. Phys. **72**, 2384 (1980).
[6] M. A. Allen and D. J. Tildesley, *Computer Simulation of Liquids* (Oxford Science, Oxford, 1987).
[7] D. Brown and J. H. R. Clarke, Mol. Phys. **51**, 1243 (1984).
[8] S. D. Bembenek, thesis dissertation, University of Kansas (August 1997).
[9] V. V. Sychev, A. A. Vasserman, A. D. Kozlov, G. A. Spiridonov, and V. A. Tsymarny, *Thermodynamic Properties of Oxygen* (Hemisphere, New York, 1987).
[10] D. McQuarrie, *Quantum Chemistry* (University Science, Mill Valley, CA, 1983), p. 164.
[11] M. Herzberg, *Molecular Spectra and Molecular Structure* (Taipei, Taiwan, 1967).

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13. ABSTRACT*(Maximum 200 words)*

Recently, we introduced a novel computer simulation technique to determine the optimal set of parameters of an interaction potential for a simple monatomic liquid. This technique was used to obtain interaction potentials of the Lennard-Jones form that accurately describe argon over its entire liquid phase at a fixed pressure (S. D. Bembenek and B. M. Rice, Mol. Phys. 97, 1085 [1999]). Here, we extend this technique to a homonuclear diatomic molecular system, liquid oxygen. This technique was first applied to a system in which the oxygen molecules were treated as point masses interacting through a modified Lennard-Jones potential. Simulations using the resulting optimal set of potential parameters of this system predict densities that are within 0.25% of experiment over the entire liquid range of oxygen at a fixed pressure. However, the errors in the internal energy and the enthalpy were as large as 9.8%. The technique was then used to determine the optimal parameters for a system of harmonic molecules, in which each molecule has two interaction sites centered at the atomic nuclei. The intermolecular interaction is the sum of all site-site interactions described by a modified Lennard-Jones potential. Simulations using these parameters reproduce experimental densities with an error no greater than 0.80%. The predictions of the internal energy and enthalpy differ from experiment by no more than 3.0% for temperatures below 90 K; predictions at 90 K differ from experiment by no more than 4.11%. These results seem to suggest that our method for determining parameters for an interaction potential is also applicable to simple molecular systems.

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