Army Research Laboratory
Aberdeen Proving Ground, MD 21005-5066

ARL-TR-2389 **February 2001**

Transitioning Model Potentials to Real Systems

Scott D. Bembenek and Betsy M. Rice
Weapons and Materials Research Directorate, ARL

Approved for public release; distribution is unlimited.

Abstract

The parameters of two pairs of potentials that describe argon over its entire liquid phase at a fixed pressure were optimized through a novel application of constant temperature and pressure molecular dynamics (*NPT*-MD) and Monte Carlo (*NPT*-MC) computer simulations. The forms of these potentials were those of a modified Lennard-Jones potential and a Lennard-Jones potential (Lennard-Jones, J. E. *Physica,* Vol. 4. p. 941, 1937). The optimized potential determined using *NPT*-MD simulations reproduced experimental densities, internal energies, and enthalpies with an error less than 1% over most of the liquid range and yielded self-diffusion coefficients that were in excellent agreement with the experiment. The results using the potential determined by *NPT*-MC simulations were in almost as good agreement with deviations from experiments of no more than 5.89% for temperatures up to vaporization. Additionally, molar volumes predicted using this potential at pressures in the 100–600 atm range and over temperatures in the 100–140 K range were within 0.83% of experimental values. These results show that when properly parameterized, Lennard-Jones-like potentials could describe a system well over a large temperature range. Further, the method introduced was easy to implement and was independent of the form of the interaction potential used.

Acknowledgments

This research was conducted while Scott D. Bembenek held a National Research Council Resident Research Associateship.

INTENTIONALLY LEFT BLANK

Table of Contents

		Page
	Acknowledgments	iii
	List of Figures	vii
	List of Tables	ix
1.	**Introduction**	1
2.	**Simulation Method**	2
2.1	Molecular Dynamics (MD)	2
2.2	Monte Carlo (MC)	6
3.	**Results**	8
3.1	Molecular Dynamics (MD)	9
3.2	Monte Carlo (MC)	13
4.	**Conclusion**	17
5.	**References**	19
	Distribution List	23
	Report Documentation Page	25

INTENTIONALLY LEFT BLANK.

List of Figures

Figure		Page
1.	Value of $< \varepsilon >/k$ and Corresponding σ for Liquid Argon at a Pressure of 40 bar for Several Temperatures	10
2.	Value of $<\varepsilon>/k$ for $\sigma = 3.40$ Å Plotted as a Function of the Cutoff Distance r_{cut} (in σ) for Liquid Argon	11
3.	Number Density of Liquid Argon (in Atoms $Å^{-3}$) as a Function of Temperature	13
4.	Internal Energy (in eV $Atom^{-1}$) as a Function of Temperature	14
5.	Enthalpy (in eV $Atom^{-1}$) as a Function of Temperature	15
6.	Value of $< \varepsilon >/k$ and Corresponding σ for Liquid Argon at a Pressure of 40 bar for Several Temperatures	16

INTENTIONALLY LEFT BLANK.

List of Tables

Table		Page
1.	The Value of $<\varepsilon>/k$ for the Common Set as a Function of Cutoff Distance Using Equation 1	10
2.	Density, Internal Energy, and Enthalpy of Liquid Argon	12
3.	Self-Diffusion Coefficients (in cm^2-s^{-1}) for Liquid Argon	15
4.	Molar Volume of Liquid Argon (in cm^3 mol^{-1})	17

INTENTIONALLY LEFT BLANK

1. Introduction

One of the major goals in any computer simulation is to accurately predict the properties of the system. This can only be accomplished with the proper choice of interaction potential. The interaction potential is a fundamental feature of a system. All thermodynamic and transport quantities will be determined by its form. Unfortunately, analytical functions, such as the hard-sphere potential, square-well potential [1] and the Lennard-Jones potential [2], provide only an approximate description of the underlying interaction potential. The Lennard-Jones potential has played an important role in the theory of classical fluids. Its simple form makes it desirable for computer simulations and theoretical calculations alike. It has been extensively used in computer simulations of liquids [3–5], glasses [6–12], and phase coexistence [13–26], to name only a few. It has also been widely used as a reference fluid in perturbation treatments for more complex fluids [27]. Further, several attempts have been made to obtain an equation of state; the most notable being by Nicolas et al. [28] and another, and more recently by Johnson et al. [29].

The Lennard-Jones potential requires only two parameters in its description: ε, which is the depth of the potential well, and σ, which is the effective particle diameter. Often, there are many parameter pairs that will predict with equal accuracy a thermodynamic property at a given phase point. However, the potentials using these different parameter sets might produce widely varying predictions at other phase points. In principle, there should be a single parameter set that will best describe the system at every phase point within the limitations of the model. In this study, this set is referred to as the "common set." This report will describe the method of finding the common set for a modified Lennard-Jones potential and a Lennard-Jones potential using either molecular dynamics or Monte Carlo simulations. It will be shown that a potential using the common set reproduces features of the system over the entire range studied. The Lennard-Jones form of the interaction potential can be regarded as one member of any number of interaction potentials that could describe the system properly over the entire liquid phase and, therefore, is not unique for parameterization using this method. In principle, this approach can

be used to optimize any functional form of the interaction potential. The method will be illustrated using liquid argon.

2. Simulation Method

The method presented can be tested by performing either Monte Carlo (MC) or molecular dynamics (MD) simulations under constant temperature and pressure.

2.1 Molecular Dynamics (MD). In MD simulations [30, 31], driving a system into a nonequilibrium steady state by coupling it to the appropriate external fields is well described [32]. These nonequilibrium molecular dynamics (NEMD) simulations allow for faster and, in some cases, more accurate determination of certain transport quantities than equilibrium simulations. A currently unexplored concept is presented here, where a nonequilibrated liquid system at constant temperature, pressure, and particle number is driven to a steady state under the constraint of achieving a particular bulk property. For this study, the bulk density was chosen to be the constraining "external field." Here, the external field will continuously "push" the system towards the desired bulk density. For these purposes, the desired density is the experimental density of liquid argon.

Consider a nonequilibrium system of N particles at constant temperature, T, and pressure, P, interacting through a modified Lennard-Jones potential,

$$v(r) = 4\varepsilon \left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6} \right] + Ar^2 + B, \tag{1}$$

where A and B are constant and chosen such that both the potential and the force are continuous at the potential cutoff, r_{cut}. Modifying the potential in this way ensures that the energy is conserved.

The bulk density constraint is imposed by starting the system with initial values of ε and σ and allowing ε to vary in time, t, according to

$$\epsilon(t) = \epsilon_0 + \lambda \sum_{t'=1}^{t} \Delta\rho(t'), \tag{2}$$

where λ is the coupling strength, ε_0 is the initial value (seed) for ε and the difference between the desired and instantaneous bulk densities is $\Delta\rho(t') \equiv \rho_{desired} - \rho(t')$. The effect is that ε will be made larger, thereby increasing the attraction between particles, if the system is "too dilute." Similarly, ε will be made smaller (thus decreasing the attraction) if the system is "too dense." A value for λ that is too large will cause the system to dramatically overshoot the desired density, thus requiring a longer amount of time for the system to relax under the "external field." The system momentum will be conserved, as in a usual equilibrium simulation, since the external field is actually coupled into the pair potential itself. Failure to conserve momentum may be further indication that the value of λ is too large. If λ is too small, the external field will be unable to compete with the fluctuations inherent in the system and, therefore, the system will never approach the desired bulk density.

Eventually, the instantaneous densities of the system will oscillate around the desired bulk density. It is necessary that the system oscillate several times around the desired bulk density before ε is chosen. This ensures that the ε that is chosen will yield the desired bulk density. In the case of liquid argon, it was found that the integration of 25,000 time steps (1 time step = 5.1 fs) was needed for the system to approach an ε that gave the desired density. After this time, an ε that reproduced the desired bulk density (for a given time step) to within a certain amount was chosen. This amount can be defined with any precision and was chosen here to be 5×10^{-6} particles $Å^{-3}$. The ability of the system to come within this established amount depends on the natural fluctuations of the system.

Repeating this procedure over a range of σ's for a given temperature and pressure will result in a set of several combinations of ε and σ' that will reproduce the desired density for this phase point. The common set, which refers to the parameter set that reproduces the density over all temperatures in the liquid phase at a given pressure, requires generating ensemble averages of ε's for the various σ's at several temperatures over the range to be studied. With the exception of simulations for which $r_{cut} = 6.00\sigma$, each ensemble consisted of ten trajectories; the remaining ensembles consisted of five trajectories. Once these parameter sets have been generated, the average value of ε, $< \varepsilon >$, for each σ is calculated and curves of $< \varepsilon >$ vs. σ for each temperature are drawn. The σ of the common set corresponds to the point where all the curves intersect (within statistical error). The ε of the common set is the average value of $< \varepsilon >$ determined for all the temperatures.

The common set obtained for the modified Lennard-Jones function in equation 1 is dependent on the value of r_{cut}. As r_{cut} becomes large, however, the changes in the common set become less pronounced, as will be shown. In order to examine this dependence on the value of r_{cut} and satisfy the minimum image convention imposed in this simulation it was necessary to increase the system size as r_{cut} increased. The systems consisted of 500; 864; 1,024; and 2,000 particles for r_{cut}'s of 2.50–3.50σ (0.025σ intervals) 4.00σ, 5.00σ, and 6.00σ, respectively. Particle masses were set to 39.95 amu, and all simulations were run at a constant pressure of 40 bar. The pressure was held constant using Andersen's method [33], 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 2×10^{-3} amu Å^{-4} for the systems consisting of 500 and 864 particles, and 5×10^{-4} amu Å^{-4} for the larger systems. Finally, the temperature was held constant through a simple scaling of velocities, and the equations of motion were integrated using a modified velocity-Verlet algorithm [30, 34, 35], which eliminated the need for scaled coordinates. The coupling strength, λ, was chosen to be 1×10^{-4} eV Å^3 particle^{-1}.

Average values for ε were determined using the procedure previously described and equation 1 with the different values of r_{cut}. Each ensemble, except for the series with $r_{cut} = 6.00\sigma$, consisted of 10 trajectories; the ensemble for $r_{cut} = 6.00\sigma$ contained 5 trajectories. The initial conditions were selected as follows: for each value of r_{cut}, σ is set to the minimum value in the range of σ's to be investigated and ε is assigned an arbitrary value. The particles were placed in lattice sites of either a bcc or fcc crystal to generate the initial coordinates. Initial velocities were set to zero, and the coordinates slightly displaced from the equilibrium lattice sites. The equations of motion were integrated for 50,000 time steps at a temperature of 135 K, and a pressure of 40 bar. This was found to be sufficient for equilibration. Once the system equilibrated, the equations of motion were then integrated for an additional 75,000 time steps, but ε was allowed to vary according to equation 2. The trajectory was stopped, and the final value of ε (denoted ε_0) and the coordinates and velocities were used as initial conditions for each trajectory with that value of r_{cut} over all the values of σ and temperature studied. It is important that a suitable ε_0 is obtained so that the system will not prematurely "vaporize" (the volume of the simulation box will expand without bound during an *NPT* simulation). The problem is circumvented by performing the equilibration of the system near the boiling point (135 K) and using the smallest value of σ (in this case, 3.35 Å) in the range. This results in the shortest attractive tail for the interaction potential (since r_{cut} is chosen to be a function of σ) over the range of σ's.

Some care must be taken not to put the system too close to the boiling point, otherwise, the system might begin to make the phase transition, which would result in a poor value for ε_0. Each trajectory to be used for $<\varepsilon>$ was integrated for 25,000 time steps beginning with the initial conditions previously described and allowing ε to vary according to equation 2. The 25,000 time steps were sufficient for the system to adjust to each new value of σ. By this time, the density of the system was oscillating about the desired value. After this period, the instantaneous density was monitored. If the instantaneous density was within 5×10^{-6} of the experimental value at that temperature and pressure, the trajectory was stopped, and the value of ε at that point was selected as the correct value for that σ value. Once this entire procedure has been performed for

the series of σ's at a single temperature, the process is repeated for that temperature, except the initial conditions for the subsequent run (coordinates and velocities) are those corresponding to the immediately preceding trajectory. This is repeated until the desired number of values of ε's that will be used in averaging are calculated for a given temperature. The σ's that were sampled ranged from 3.35–3.45 Å (in increments of 0.025 Å) and the temperatures sampled ranged from 85–145 K (in intervals of 5 K). Once the set of ε's and σ's have been determined for all of the temperatures, the common set can be obtained by superimposing plots of the curves showing $<\varepsilon>$ vs. σ for all temperatures sampled in the study.

In order to evaluate the performance of the modified Lennard-Jones potential using the common set obtained for $r_{cut} = 6.00\sigma$, time averages of bulk properties of the liquid over the temperature range 85–145 K were calculated. For each temperature, a trajectory consisting of 250,000 time steps was integrated to generate the ensemble averages. The initial coordinates and velocities of a system of 2,000 particles were generated by first setting up the particles in an bcc lattice, and performing a trajectory integration for 50,000 time steps at the desired temperature and pressure, using equation 1 and $r_{cut} = 6.00\sigma$. The ensemble averages were obtained by averaging over the calculated values for the remaining 200,000 time steps.

2.2 Monte Carlo (MC). This technique can be implemented using MC simulations as well. MC does not require continuous forces at the cutoff distance; therefore, this method will be demonstrated using the unmodified Lennard-Jones potential. Long-range corrections are included to account for all interactions of pairs whose distances exceed r_{cut} [30, 31]. The density constraint can be implemented in the same way as was done for MD using equation 2. However, the time dependence in equation 2 is not applicable to MC, and therefore, it is replaced with a "step" dependence,

$$\epsilon_{\text{step}} = \varepsilon_0 + \lambda \sum_{i=1}^{step} \Delta \rho^i , \qquad (3)$$

where λ is the coupling strength as previously described, ε_{step} is the value for ε for that step of the Markov sequence, ε_0 is the initial value for ε and $\Delta\rho_i$ is the difference between the desired and instantaneous bulk densities.

Parameter sets for various values of σ over the temperature range 85–145 K were determined using *NPT*-MC simulations and equation 3. As in the MD simulations, these sets were determined for σ values ranging from 3.35–3.45 Å in increments of 0.025 Å. The simulation box contained 150 atoms, placed randomly within the box, and the size of the box was initially set such that the initial density was equal to the experimental value at 135 K, 40 bar. As in the MD simulations, σ is set to the minimum value in the range to be studied, and ε is given an arbitrary value. The *NPT*-MC simulation proceeded for 100,000 moves, with ε remaining fixed. This was sufficient to equilibrate the system to the desired thermodynamic state. Imposing the same temperature and pressure constraints, the *NPT*-MC simulation proceeded for an additional 100,000 Markov moves but the ε was now allowed to vary according to equation 3. The sequence continued with a trial move of the particle positions, which generated an instantaneous density. A new value of ε was generated according to equation 3. The energy of the system using the new value of ε was calculated, and the changes accepted or rejected according to the probability min [1, exp (−W/kT)] [30, 31] where

$$W = P(V_{new} - V_{old}) + (U_{new} - U_{old}) + NkT\ln\frac{V_{old}}{V_{new}}, \tag{4}$$

and P, V, and U denote the pressure, volume, and potential energy of the system, respectively. The magnitude of the displacements of the particles during the Markov sequence were chosen such that 50% of all attempted moves were accepted. If a trial move was rejected, the properties associated with the immediately preceding configuration were included for averaging.

The final value of ε at the end of the 100,000 moves became ε_0 and the resulting coordinates were used for the initial conditions for *NPT*-MC calculations to determine ε as a function of σ over the entire liquid phase at 40 bar. As in the MD simulations, this process is repeated for the

series of σ's at each temperature, except that the initial conditions for the subsequent run (coordinates) are those corresponding to the final configuration of the immediately preceding Markov sequence. This is repeated five times in this study. The common set is determined, as before, by superimposing the plots of $< \varepsilon >$ vs. σ for each temperature.

In order to assess the performance of the Lennard-Jones potential using this set of parameters and those derived from other studies [36, 37], *NPT*-MC simulations of liquid argon at 40 bar over the temperature range 85–145 K were performed. The initial system consisted of 108 atoms in a cubic box where each edge length was 17.46 Å. Periodic boundary conditions were imposed, and a cutoff distance equal to one-half of the edge of the box was used. Long-range corrections to the calculations were included. An initial equilibration simulation using the Lennard-Jones parameters of Wijker et al. [37] for T = 97 K, P = 17 atm was performed in order to reproduce one of the values generated by McDonald and Singer [36]. An excess of 500,000 Markov moves were used for equilibration, and 100,000 moves were used in averaging the results. The results using this parameter set were reproduced. This coordinate set was then used as the initial set for the calculations of properties at 85 K using parameters obtained in this work, from McDonald and Singer [36], and from Wijker et al. [37]. An equilibration Markov sequence of 10,000 steps was performed at T = 85 K, P = 40 bar and thermodynamic properties were calculated and averaged over the next 100,000 steps. A new temperature was then selected, and the process repeated until the entire temperature range had been sampled. Longer Markov chains were generated, and different sequences were initiated, but the results did not vary.

3. Results

Although argon has been well described using more complex interaction potentials [38, 39] the purposes of this study are (1) to illustrate the newly described method for obtaining parameter sets using either MD or MC, and (2) to show that the Lennard-Jones potential can obtain accurate results over the entire liquid phase upon proper parameterization.

3.1 Molecular Dynamics (MD). Parameters for the modified Lennard-Jones potential (equation 1) were determined using the method described in the preceding section for temperatures of 85–145 K. The value of $<\varepsilon>/k$ and the corresponding σ for liquid argon at a pressure of 40 bar at several temperatures is shown in Figure 1. This is presented for cutoffs r_{cut}'s of 2.50σ and 6.00σ. Figure 1(a) shows $<\varepsilon>/k$ vs. σ using $r_{cut} = 2.50\sigma$, and Figure 1(b) shows the values using $r_{cut} = 6.00\sigma$. In the figure, the common set corresponds where all of the curves intersect (within statistical error). This changes considerably from 2.50σ until about 4.00σ, where it slowly converges to its value at 6.00σ. The common set at 6.00σ was used to calculate all properties of interest for the MD simulations. The error bars for all points are on the order of the size of the symbols except for those points at 145 K, which show the error bars explicitly. The deviations at 145 K are due to the proximity of the system to the boiling point; the system is beginning to make the expected phase transition. Since the values generated at 145 K have such greater uncertainty than the remaining points, these have not been included in the determination of the common set. For all values of r_{cut}, the σ in the common set is 3.40 Å but the corresponding ε values are very different. For example, for $r_{cut} = 2.50\sigma$, the value of $<\varepsilon>/k$ is 155.876 K, but the value of $<\varepsilon>/k$ resulting from the simulations in which $r_{cut} = 6.00\sigma$ is 119.808 K. The changes in the value of the ε of the common sets with increasing values of r_{cut} are given in Table 1, and illustrated in Figure 2. The values of ε for the common set appear to be converging as r_{cut} increases (i.e., $<\varepsilon>/k$ converges for $\sigma = 3.40$ Å to ≈ 120 K as r_{cut} is extended). The error bars have been eliminated since they are comparable with the size of the symbols.

The performance of the modified Lennard-Jones potential using the common set obtained for $r_{cut} = 6.00\sigma$ was tested, in order to keep the system size small enough that molecular simulation would not be computationally prohibitive. *NPT*-MD simulations were used to calculate ensemble averages for density, internal energy and enthalpy over the temperature range 85–145 K at 40 bar. Table 2 gives the calculated ensemble averages for densities, internal energies and enthalpies along with the experimental values [40], and the comparisons are illustrated in Figures 3–5, each of which are based on MC calculations using the parameters of Wijker et al. [37], McDonald and Singer [36], and those obtained in this work along with the

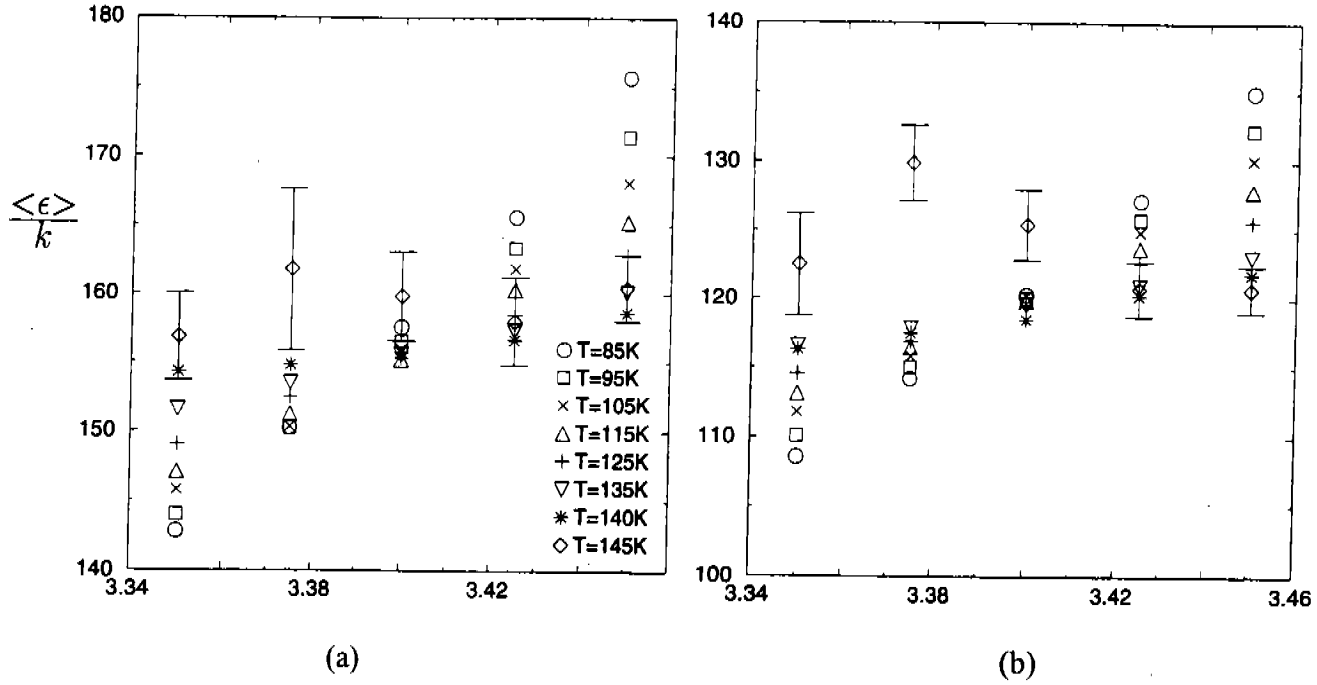

Figure 1. Value of < ε >/k and Corresponding σ for Liquid Argon at a Pressure of 40 bar for Several Temperatures.

Table 1. Value of <ε>/k for the Common Set as a Function of Cutoff Distance Using Equation 1

$r_{cut}(\sigma)$[a]	(<ε>/k)/K	Deviation
2.50	155.876	0.161
2.75	144.707	0.126
3.00	137.652	0.115
3.25	133.112	0.171
3.50	129.875	0.184
4.00	125.437	0.116
5.00	121.516	0.069
6.00	119.808	0.088

[a]The value of σ for the common set is 3.40 Å.

experimental values [40]. Also shown in Figures 3–5 are the values obtained from MD simulations using the parameters found in this work. The error bars have been eliminated since they are comparable to the size of the symbols. The density (Figure 3), the energy (Figure 4),

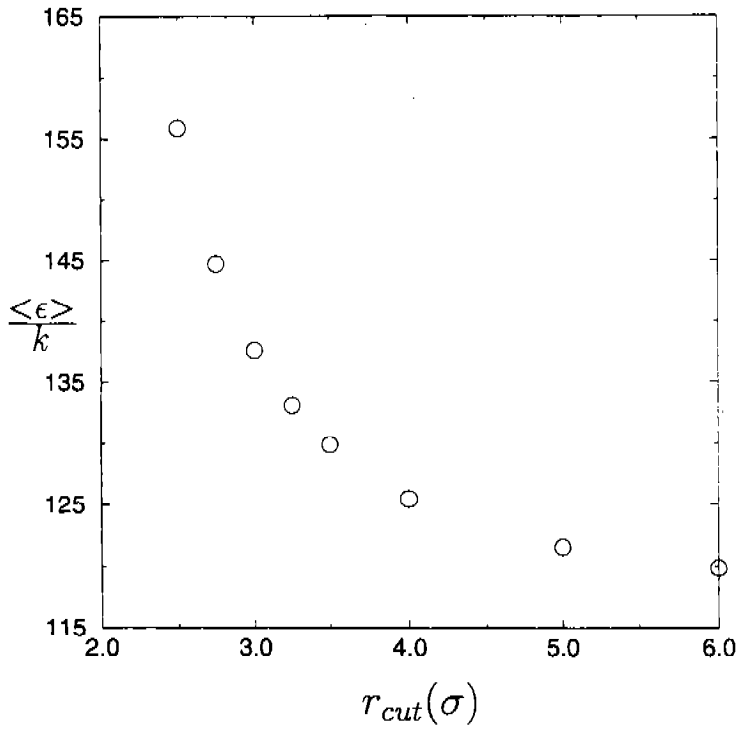

Figure 2. Value of <ε>/k for σ = 3.40 Å Plotted as a Function of the Cutoff Distance r_{cut} (in σ) for Liquid Argon.

and the enthalpy (Figure 5) have been multiplied by 10^2 for convenience. The calculated results are within 1% of the experimental data for most of the results over the temperature range investigated. (Once again, the deviations at 145 K result from the system being at the boiling point.) These results are comparable with results that were obtained with a more complicated interaction potential [39].

The ability of the modified Lennard-Jones potential using the common set obtained at r_{cut} = 6.00σ to describe the self-diffusion coefficient has also been evaluated. In their paper [41], Naghizadeh and Rice present experimental data of self-diffusion for liquid argon over a temperature range of 90–120 K for pressures of 12.9, 57.5, 103.0, and 135.0 atm. The behavior of the self-diffusion coefficients with temperature at each pressure was satisfactorily described using an Arrhenius-like expression. Naghizadeh and Rice fitted their data to this expression, and provided an analytical description of the temperature dependence of the self-diffusion coeffcient for liquid argon could be estimated at a pressure of 40 bar for each temperature, to allow for a comparison with the MD simulations results.

Table 2. Density, Internal Energy, and Enthalpy of Liquid Argon

	$\rho/10^2$ atoms Å^{-3}					$-U/10^2$ eV atom^{-1}					$-H/10^2$ eV atom^{-1}				
				This work					This work					This work	
T/K	Expt.	McDonald and Singer[a]	Wijker et al.[b]	MC	MD	Expt.	McDonald and Singer[a]	Wijker et al.[b]	MC	MD	Expt	McDonald and Singer[a]	Wijker et al[b]	MC	MD
85	2.1388	2.1495	2.1667	2.1513	2.1334	5.024	5.094	5.296	5.022	5.048	4.907	4.978	5.181	4.906	4.931
90	2.0933	2.0976	2.1169	2.1039	2.0877	4.807	4.844	5.048	4.789	4.821	4.688	4.725	4.930	4.670	4.701
95	2.0467	2.0475	2.0681	2.0541	2.0413	4.584	4.602	4.804	4.551	4.593	4.462	4.480	4.684	4.429	4.471
100	1.9989	1.9987	2.0257	2.0041	1.9939	4.357	4.368	4.587	4.316	4.364	4.232	4.242	4.464	4.191	4.239
105	1.9488	1.9477	1.9680	1.9501	1.9443	4.124	4.129	4.323	4.069	4.132	3.996	4.001	4.196	3.940	4.003
110	1.8966	1.8930	1.9232	1.8972	1.8933	3.887	3.881	4.101	3.829	3.897	3.754	3.749	3.971	3.697	3.765
115	1.8410	1.8368	1.8640	1.8336	1.8382	3.643	3.632	3.838	3.562	3.652	3.507	3.496	3.704	3.425	3.516
120	1.7816	1.7786	1.8151	1.7750	1.7806	3.392	3.380	3.609	3.309	3.403	3.252	3.240	3.471	3.168	3.263
125	1.7167	1.7158	1.7491	1.7126	1.7199	3.130	3.120	3.329	3.052	3.149	2.985	2.974	3.186	2.906	3.004
130	1.6442	1.6414	1.6840	1.6416	1.6514	2.855	2.828	3.060	2.772	2.875	2.703	2.675	2.911	2.619	2.724
135	1.5601	1.5708	1.6146	1.5539	1.5719	2.551	2.550	2.779	2.453	2.575	2.391	2.390	2.624	2.292	2.416
140	1.4567	1.4683	1.5358	1.4490	1.4781	2.208	2.190	2.474	2.090	2.243	2.037	2.020	2.311	1.917	2.074
145	1.3079	1.1768	1.4237	0.8717	1.3520	1.770	1.356	2.086	0.542	1.837	1.579	1.091	1.909	0.114	1.652

[a][36]
[b][37]

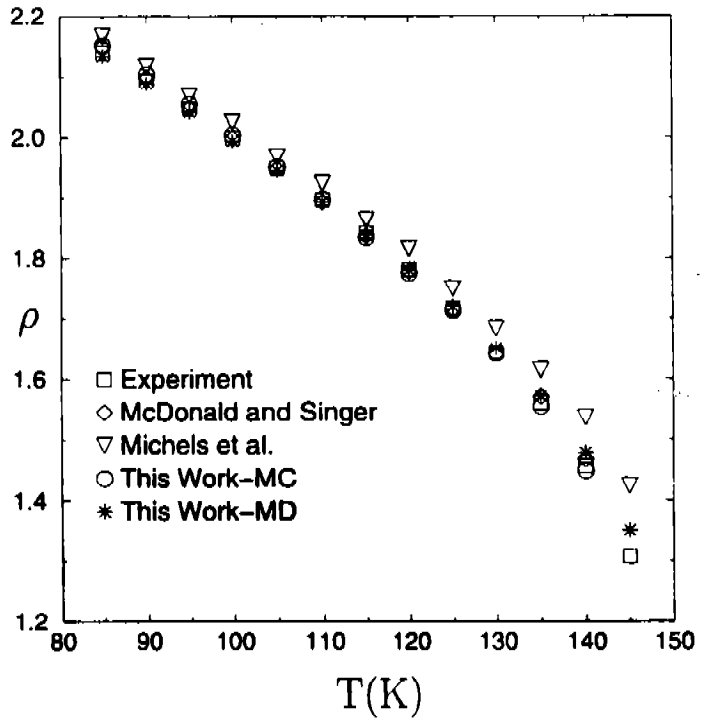

Figure 3. Number Density of Liquid Argon (in Atoms Å^{-3}) as a Function of Temperature.

The self-diffusion coefficient from MD is calculated from the mean-square displacement and is an average over ten trajectories each consisting of 20,000 integration steps. Table 3 compares the experimental and calculated self-diffusion coefficients as a function of temperature. The calculated values have a larger percentage deviation (with a maximum error of 8%) from experimental values than those of the thermodynamic properties, but are still in reasonably good agreement. However, Naghizadeh and Rice indicate that their data contains uncertainties of less than 5%, which could account for some of the discrepancies.

3.2 Monte Carlo (MC). Lennard-Jones parameters for liquid argon were obtained using the method described in section 2 and *NPT*-MC calculations over the temperature range 85–145 K, at 40 bar. Figure 6 shows $<\varepsilon>/k$ over the σ range 3.35–3.45 Å in increments of 0.025 Å obtained from *NPT*-MC calculations using this method. In this figure, the common set corresponds to σ = 3.40 Å as it did in the application of the method using *NPT*-MD. The value of ε, averaged over all temperatures is $<\varepsilon>/k$ = 116.359 ± 0.128 K. The value for ε is 3% smaller than that obtained by Wijker et al. [37] and is within the error of the value given by

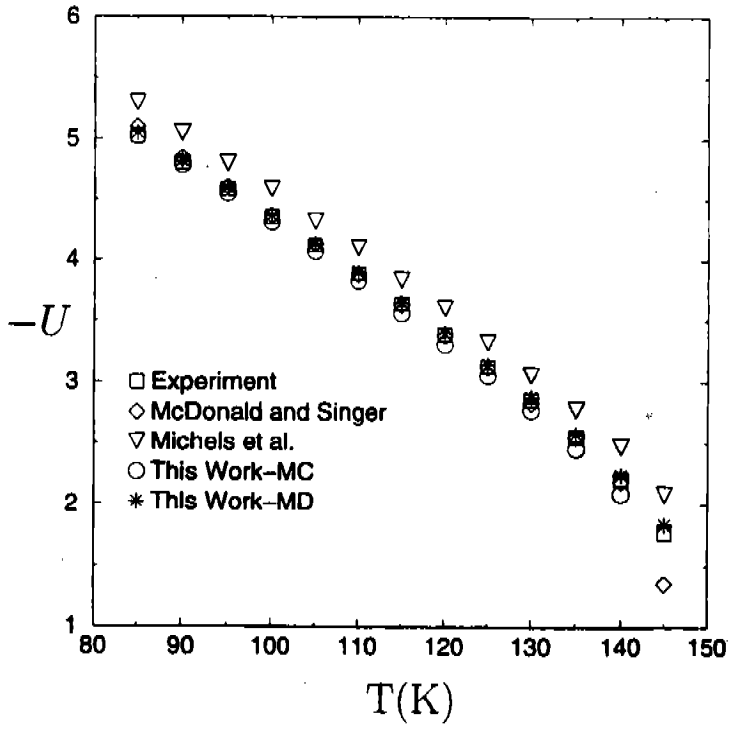

Figure 4. Internal Energy (in eV Atom^{-1}) as a Function of Temperature.

McDonald and Singer (117.2 K ± 1.4 K) [36]. The value for σ that was calculated is close to that of Wijker et al. [37] and McDonald and Singer (3.40 Å) [36]; however, when generating the curves of ε as a function of σ at each temperature, those for a fine grid of σ values were not. Rather, these points were generated at intervals of 0.025 Å.

The parameters of Wijker et al. [37] were obtained using experimental gas-phase information for argon, rather than liquid state information. Small discrepancies between experiment and results from constant volume and temperature (*NVT*)-MC simulations using these parameters to describe thermodynamic properties in the liquid state led McDonald and Singer to propose a new set of parameters that would better reproduce values in the liquid state [36]. In order to compare the results described herein with those of experiment (Wijker et al. [37] and McDonald and Singer [36]), *NPT*-MC simulations were performed to predict densities, internal energies and enthalpies for liquid argon at 40 bar, over the temperature range 85–145 K using Lennard-Jones potentials with the parameters of McDonald and Singer [36], Wijker et al. [37], and the set that

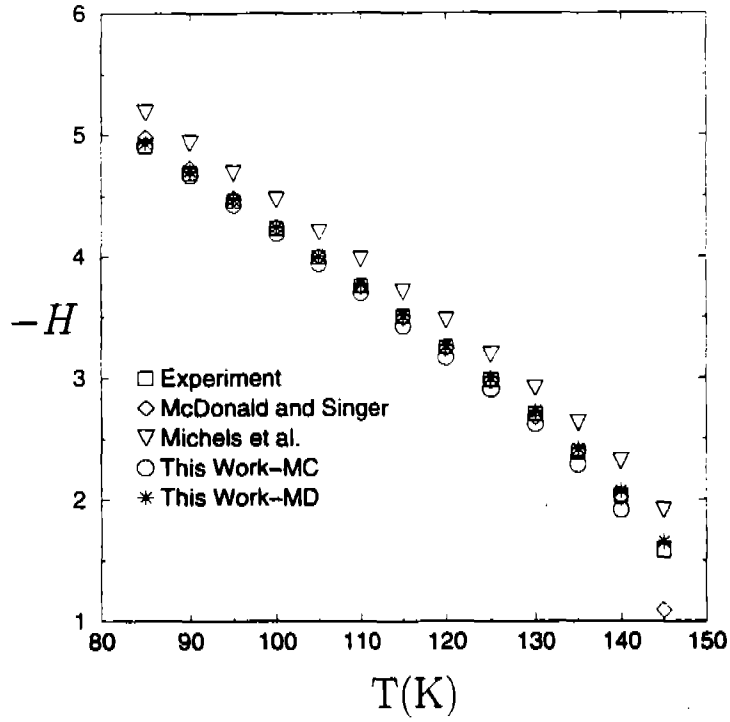

Figure 5. Enthalpy (in eV Atom^{-1}) as a Function of Temperature.

Table 3. Self-Diffusion Coefficients (in cm^2-s^{-1}) for Liquid Argon

T/K	D_{exp} H 10^5	D_{MD} H 10^5
85	1.681	1.783
90	2.122	2.281
95	2.614	2.709
100	2.954	3.191
105	3.737	3.764
110	4.361	4.533
115	5.022	5.374
120	5.715	5.950

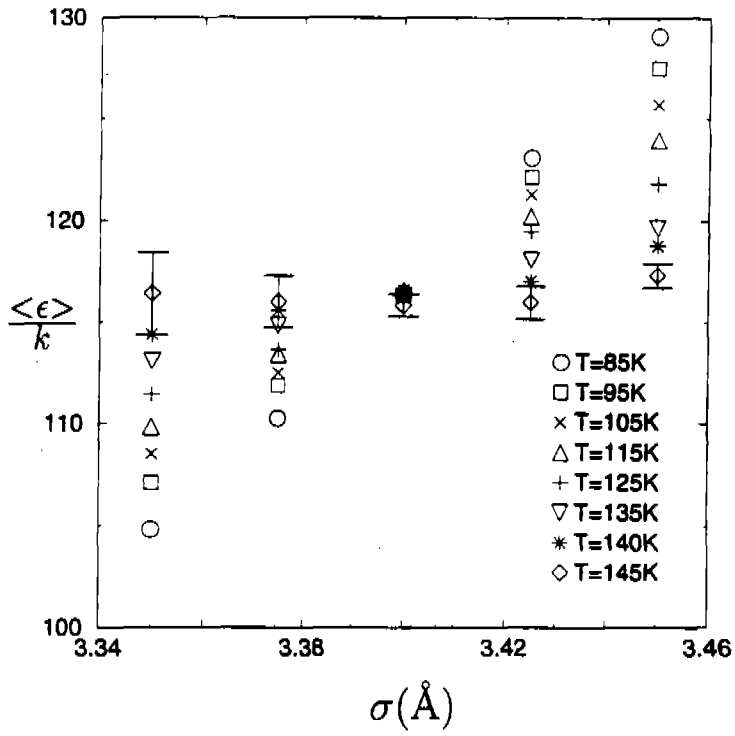

Figure 6. The Value of < ε >/k and Corresponding σ for Liquid Argon at a Pressure of 40 bar for Several Temperatures.

was derived using the method described in this work. The results of all calculations are given in Table 2 for comparison with experiment and among the predicted values; Figures 3–5 provide visual comparisons. With the exception of values at 145 K, the calculations using the Wijker et al. [37] set are in poorer agreement with experiment than potentials using the set derived herein or the McDonald and Singer set [36]. Properties calculated at 145 K using both the McDonald and Singer set and the parameters determined in this work have a significant deviation from experimental values. The values, however, do not represent an average over a single phase since the system is actually fluctuating between the liquid and vapor states [30], which was evident upon inspection of the instantaneous densities. At temperatures away from this phase transition, the properties predicted using either McDonald and Singer or our set are comparable, thus affirming McDonald and Singer's conclusion that the parameters generated by Wijker et al. produce an attractive well too deep for liquid argon [36].

The parameters generated in this work were determined using experimental information of the density of liquid argon at 40 bar; in order to assess the performance of this potential at other pressures, *NPT*-MC calculations were performed at pressures ranging from 100–600 atm, at 100, 120, and 140 K for comparison with experiment. The resulting molar volumes are given in Table 4 and compared with the experimental results of Streett and Staveley [42]. The predicted values over the entire pressure and temperature range are in agreement with experiment to 0.83%.

Table 4. Molar Volume of Liquid Argon (in $cm^3\ mol^{-1}$)

	T/K					
P/atm	100.0		120.0		140.0	
	Experiment	This work	Experiment	This work	Experiment	This work
100.0	29.69	29.64	32.77	32.88	37.49	37.80
200.0	29.01	28.94	31.52	31.66	34.91	35.11
300.0	28.46	28.35	30.62	30.70	33.20	33.44
400.0	27.98	27.88	29.91	29.93	32.14	32.27
500.0	27.57	27.47	29.33	29.30	31.27	31.35
600.0	27.23	27.08	28.82	28.83	30.58	30.66

4. Conclusion

It has been shown that it is possible to optimize a pair-additive interaction potential using molecular simulations in which the system is constrained to reproduce the experimental bulk property over a range of temperatures at a constant pressure. Specifically, this was shown for liquid argon using either a modified or unmodified Lennard-Jones potential, and using the bulk density of the liquid as the constraining factor. The modification to the Lennard-Jones potential used in the *NPT*-MD simulations was made to conserve the energy during the trajectory integration and to ensure the force was continuous at the cutoff distance. Since *NPT*-MC

simulations do not require this, application of the method using *NPT*-MC was performed using a regular Lennard-Jones interaction potential with cutoff.

NPT-MD simulations using this method produced values of $<\varepsilon>/k$ = 119.808 K and σ = 3.40 Å with r_{cut} of 6.00σ were found to be the best set of parameters over the temperature range of 85–145 K. Using these parameters, excellent agreement with experiment for density, internal energy, enthalpy, and self-diffusion coefficient was obtained. This suggests that density is a good constraint. *NPT*-MC simulations using this method produced values of $<\varepsilon>/k$ = 116.237 K and σ = 3.40 Å for the unmodified Lennard-Jones potential, which also gave results that were in very good agreement with experiment over the temperature range.

Results from the simulations using either *NPT*-MD and *NPT*-MC were compared against available experimental information and *NPT*-MC calculations using parameters for the Lennard-Jones potential suggested by McDonald and Singer [36] and Wijker et al. [37]. The results using the parameters generated in this study were in better agreement with experiment than those using the Wijker et al. set, and were comparable to those generated using the McDonald and Singer results. Additionally, *NPT*-MC calculations were performed using the common set of parameters determined for the Lennard Jones potential for temperatures ranging 100–140 K and pressures of 100–600 atm for comparison with experimental results. The molar volumes calculated using *NPT*-MC were within 0.83% of the experimental values. The results presented herein seemed to indicate that ε and σ are independent of temperature and pressure.

Although this method should be applied to other systems to determine if it will show the same degree of success in parameterizing simple potential energy functions, the results herein suggest that this might be a very useful and powerful tool for easily and effectively developing model interaction potentials to describe real systems. Such models can then be used to obtain thermodynamic and some transport properties from computer simulations.

5. References

1. Hirschfelder, J. O., C. F. Curtiss, and R. B. Bird. *Molecular Theory of Gases and Liquids*. New York, NY: Wiley, 1964.

2. Lennard-Jones, J. E. *Physica*. Vol. 4, p. 941, 1937.

3. Verlet, L. *Physical Review*. Vol. 159, p. 98, 1967.

4. Buchner, M., B. M. Ladanyi, and R. M. Stratt. *Journal of Chemical Physics*. Vol. 97, p. 8522, 1992.

5. Larsen, R. E., G. Goodyear, and R. M. Stratt. *Journal of Chemical Physics*. Vol. 104, p. 2987, 1995.

6. Madsen, J. U., and R. M. J. Cotterill. *Physics Letters*. Vol. 83A, p. 219, 1981.

7. Keyes, T. *Journal of Chemical Physics*. Vol. 101, p. 5081, 1994.

8. Vollmayr, K., W. Kob, and K. Binder. *Europhysics Letters*. Vol. 32, p. 715, 1995.

9. Vollmayr, K., W. Kob, and K. Binder. *Physical Review B*. Vol. 54, p. 15808, 1996.

10. Bembenek, S. D., and B. B. Laird. *Physical Review Letters*. Vol. 74, p. 936, 1995.

11. Bembenek, S. D., and B. B. Laird. *Journal of Chemical Physics*. Vol. 104, p. 1, 1996.

12. Laird, B. B., and S. D. Bembenek. *Journal of Physics: Condensed Matter*. Vol. 8, p. 9569, 1996.

13. Hansen, J., and L. Verlet. *Physical Review*. Vol. 184, p. 151, 1969.

14. Liu, K. S. *Journal of Chemical Physics*. Vol. 60, p. 4226, 1974.

15. Ladd, A. J. C., and L. V. Woodcock. *Chemical Physics Letters*. Vol. 51, p. 155, 1977.

16. Toxvaerd, S., and E. Praestgaard. *Journal of Chemical Physics*. Vol. 67, p. 5291, 1977.

17. Hiwatari, Y., E. Stoll, and T. Schneider. *Journal of Chemical Physics*. Vol. 68, p. 3401, 1978.

18. Ladd, A. J. C., and L. V. Woodcock. *Journal of Physics C*. Vol. 11, p. 3565, 1978.

19. Bonissent, A., E. Gauthier, and J. L. Finney. *Philosophical Magazine*. Vol. 39, p. 49, 1979.

20. Bushnell-Wye, G. M., J. L. Finney, and A. Bonissent. *Philosophical Magazine*. Vol. 44, p. 1053, 1981.

21. Broughton, J. Q., and G. H. Gilmer. *Journal of Chemical Physics*. Vol. 84, p. 5741, 1986.

22. Broughton, J. Q., and G. H. Gilmer. *Journal of Chemical Physics*. Vol. 84, p. 5749, 1986.

23. Broughton, J. Q., and G. H. Gilmer. *Journal of Chemical Physics*. Vol. 84, p. 5759, 1986.

24. Nijmeijer, M. J. P., A. F. Bakker, C. Bruin, and J. H. Sikkenk. *Journal of Chemical Physics*. Vol. 89, p. 3789, 1988.

25. Holcomb, C. D., P. Clancy, S. M. Thompson, and J. A. Zollweg. *Fluid Phase Equilibria*. Vol. 75, p. 185, 1992.

26. Lotfi, A., J. Vrabec, and J. Fischer. *Molecular Physics*. Vol. 76, p. 1319, 1992.

27. Barker, J. A., and D. Henderson. *Reviews of Modern Physics*. Vol. 48, p. 587, 1976.

28. Nicolas, J. J., K. E. Gubbins, W. B. Street, and D. J. Tildesley. *Molecular Physics*. Vol. 37, p. 1429, 1979.

29. Johnson, K., J. A. Zollweg, and K. E. Gubbins. *Molecular Physics*. Vol. 78, p. 591, 1993.

30. Allen, M. A., and D. J. Tildesley. *Computer Simulation of Liquids*. Oxford, England: Clarendon Press, 1987; Collaborative Computational Projects-5 (CCP5) Newsletter, no. 31, October 1989 (see http://www.dl.ac.uk/CCP/CCP5/newsletter_index.html).

31. Frenkel, D., and B. Smit. *Understanding Molecular Simulations*. London, England: Academic Press, 1996.

32. Evans, D. J., and G. P. Morriss. *Computational Physics Reports*. Vol. 1, p. 297, 1984.

33. Andersen, H. C. *Journal of Chemical Physics*. Vol. 72, p. 2384, 1980.

34. Brown, D., and J. H. R. Clarke. *Molecular Physics*. Vol. 51, p. 1243, 1984.

35. Bembenek, S. D. Ph.D. Dissertation, University of Kansas, Lawrence, KS, August 1997.

36. McDonald, I. R., and K. Singer. *Journal of Chemical Physics*. Vol. 50, p. 2308, 1969.

37. Wijker, H., A. Michels, and H. K. Wijker. *Physica*. Vol. 15, p. 627, 1949.

38. Barker, J. A., R. A. Fisher, and R. O. Watts. *Molecular Physics*. Vol. 21, p. 657, 1971.

39. Miyano, Y. *Fluid Phase Equilibria*. Vol. 95, p. 31, 1994.

40. Sychev, V. V., A. A. Vasserman, A. D. Kozlov, G. A. Spiridonov, and V. A. Tsymarny. *Thermodynamic Properties of Neon, Argon, Krypton, and Xenon*. New York, NY: Hemisphere, 1987.

41. Naghizadeh, J., and S. A. Rice. *Journal of Chemical Physics*. Vol. 36, p. 2710, 1962.

42. Streett, W. B., and L. A. K. Staveley. *Journal of Chemical Physics*. Vol. 50, p. 2302, 1969.

INTENTIONALLY LEFT BLANK.

NO. OF COPIES	ORGANIZATION
2	DEFENSE TECHNICAL INFORMATION CENTER DTIC DDA 8725 JOHN J KINGMAN RD STE 0944 FT BELVOIR VA 22060-6218
1	HQDA DAMO FDT 400 ARMY PENTAGON WASHINGTON DC 20310-0460
1	OSD OUSD(A&T)/ODDDR&E(R) R J TREW THE PENTAGON WASHINGTON DC 20301-7100
1	DPTY CG FOR RDA US ARMY MATERIEL CMD AMCRDA 5001 EISENHOWER AVE ALEXANDRIA VA 22333-0001
1	INST FOR ADVNCD TCHNLGY THE UNIV OF TEXAS AT AUSTIN PO BOX 202797 AUSTIN TX 78720-2797
1	DARPA B KASPAR 3701 N FAIRFAX DR ARLINGTON VA 22203-1714
1	US MILITARY ACADEMY MATH SCI CTR OF EXCELLENCE MADN MATH MAJ HUBER THAYER HALL WEST POINT NY 10996-1786
1	DIRECTOR US ARMY RESEARCH LAB AMSRL D D R SMITH 2800 POWDER MILL RD ADELPHI MD 20783-1197

NO. OF COPIES	ORGANIZATION
1	DIRECTOR US ARMY RESEARCH LAB AMSRL DD 2800 POWDER MILL RD ADELPHI MD 20783-1197
1	DIRECTOR US ARMY RESEARCH LAB AMSRL CI AI R (RECORDS MGMT) 2800 POWDER MILL RD ADELPHI MD 20783-1145
3	DIRECTOR US ARMY RESEARCH LAB AMSRL CI LL 2800 POWDER MILL RD ADELPHII MD 20783-1145
1	DIRECTOR US ARMY RESEARCH LAB AMSRL CI AP 2800 POWDER MILL RD ADELPHI MD 20783-1197
	ABERDEEN PROVING GROUND
4	DIR USARL AMSRL CI LP (BLDG 305)

NO. OF COPIES	ORGANIZATION
	ABERDEEN PROVING GROUND
21	DIR USARL AMSRL WM B RINGERS AMSRL WM BD B E FORCH W R ANDERSON S W BUNTE C F CHABALOWSKI A COHEN R DANIEL D DEVYNCK R A FIFER B E HOMAN A J KOTLAR K L MCNESBY M MCQUAID M S MILLER A W MIZIOLEK J B MORRIS R A PESCE-RODRIGUEZ B M RICE R C SAUSA M A SCHROEDER J A VANDERHOFF

REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302, and to the Office of Management and Budget, Paperwork Reduction Project(0704-0188), Washington, DC 20503.

1. AGENCY USE ONLY *(Leave blank)*	2. REPORT DATE	3. REPORT TYPE AND DATES COVERED
	February 2001	October 1997 - October 1998

4. TITLE AND SUBTITLE
Transitioning Model Potentials to Real Systems

5. FUNDING NUMBERS
622618.H80

6. AUTHOR(S)
Scott D. Bembenek and Betsy M. Rice

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)
U.S Army Research Laboratory
ATTN: AMSRL-WM-BD
Aberdeen Proving Ground, MD 21005-5066

8. PERFORMING ORGANIZATION REPORT NUMBER
ARL-TR-2389

9. SPONSORING/MONITORING AGENCY NAMES(S) AND ADDRESS(ES)

10.SPONSORING/MONITORING AGENCY REPORT NUMBER

11. SUPPLEMENTARY NOTES

12a. DISTRIBUTION/AVAILABILITY STATEMENT
Approved for public release; distribution is unlimited.

12b. DISTRIBUTION CODE

13. ABSTRACT*(Maximum 200 words)*

The parameters of two pairs of potentials that describe argon over its entire liquid phase at a fixed pressure were optimized through a novel application of constant temperature and pressure molecular dynamics (*NPT*-MD) and Monte Carlo (*NPT*-MC) computer simulations. The forms of these potentials were those of a modified Lennard-Jones potential and a Lennard-Jones potential (Lennard-Jones, J. E. *Physica*, Vol. 4, p. 941, 1937). The optimized potential determined using *NPT*-MD simulations reproduced experimental densities, internal energies, and enthalpies with an error less than 1% over most of the liquid range and yielded self-diffusion coefficients that were in excellent agreement with the experiment. The results using the potential determined by *NPT*-MC simulations were in almost as good agreement with deviations from experiments of no more than 5.89% for temperatures up to vaporization. Additionally, molar volumes predicted using this potential at pressures in the 100–600 atm range and over temperatures in the 100–140 K range were within 0.83% of experimental values. These results showed that when properly parameterized, Lennard-Jones-like potentials could describe a system well over a large temperature range. Further, the method introduced was easy to implement and was independent of the form of the interaction potential used.

14. SUBJECT TERMS
molecular dynamics, Monte Carlo, oxygen, intermolecular potential

15. NUMBER OF PAGES
30

16. PRICE CODE

17. SECURITY CLASSIFICATION OF REPORT	18. SECURITY CLASSIFICATION OF THIS PAGE	19. SECURITY CLASSIFICATION OF ABSTRACT	20. LIMITATION OF ABSTRACT
UNCLASSIFIED	UNCLASSIFIED	UNCLASSIFIED	UL

NSN 7540-01-280-5500

Standard Form 298 (Rev. 2-89)
Prescribed by ANSI Std. 239-18 298-102

INTENTIONALLY LEFT BLANK.

USER EVALUATION SHEET/CHANGE OF ADDRESS

This Laboratory undertakes a continuing effort to improve the quality of the reports it publishes. Your comments/answers to the items/questions below will aid us in our efforts.

1. ARL Report Number/Author ARL-TR-2389 (Bembenek) Date of Report February 2001

2. Date Report Received _____

3. Does this report satisfy a need? (Comment on purpose, related project, or other area of interest for which the report will be used.) _____

4. Specifically, how is the report being used? (Information source, design data, procedure, source of ideas, etc.) _____

5. Has the information in this report led to any quantitative savings as far as man-hours or dollars saved, operating costs avoided, or efficiencies achieved, etc? If so, please elaborate. _____

6. General Comments. What do you think should be changed to improve future reports? (Indicate changes to organization, technical content, format, etc.) _____

CURRENT ADDRESS

Organization

Name E-mail Name

Street or P.O. Box No.

City, State, Zip Code

7. If indicating a Change of Address or Address Correction, please provide the Current or Correct address above and the Old or Incorrect address below.

OLD ADDRESS

Organization

Name

Street or P.O. Box No.

City, State, Zip Code

(Remove this sheet, fold as indicated, tape closed, and mail.)

(DO NOT STAPLE)

DEPARTMENT OF THE ARMY

OFFICIAL BUSINESS

NO POSTAGE NECESSARY IF MAILED IN THE UNITED STATES

BUSINESS REPLY MAIL

FIRST CLASS PERMIT NO 0001,APG,MD

POSTAGE WILL BE PAID BY ADDRESSEE

DIRECTOR
US ARMY RESEARCH LABORATORY
ATTN AMSRL WM BD
ABERDEEN PROVING GROUND MD 21005-5066