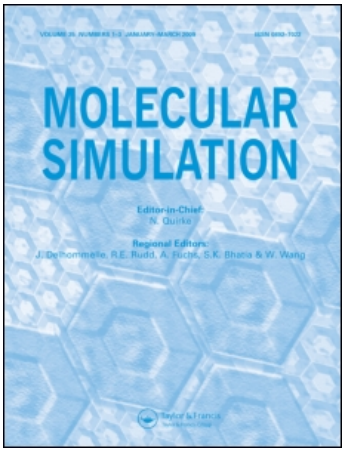

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Monte Carlo Study of the Buckingham Exponential-six Fluid

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MONTE CARLO STUDY OF THE BUCKINGHAM EXPONENTIAL-SIX FLUID

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In this paper we report the results of extensive Monte Carlo simulations of a pure fluid of Buckingham modified exponential-six molecules. Data are presented for the configurational energy and pressure covering a wide range of temperatures and densities. These data are interpreted using the generalized van der Waals partition function with a novel separation into free volume and mean potential terms. We find, surprisingly, that the Buckingham fluid is described by a simple van der Waals-like equation of state provided that the b parameter is temperature dependent and chosen in a theoretically correct manner.

KEY WORDS: Buckingham potential, Monte Carlo simulation, van der Waals equation of state, van der Waals partition function.

1 INTRODUCTION

The correlation of phase equilibrium data, or its prediction when data are not available, is an important step in process design. To accomplish such calculations, accurate thermodynamic models are needed. While many thermodynamic models are based on empiricism, we have instead been using statistical mechanical theory and Monte Carlo computer simulation as the starting points for the development of theoretically-based equations of state, their mixing rules and activity coefficient models. The basis for our effort is the generalized van der Waals partition function; it is the formalism that allows us to make the transition between molecular-level assumptions and thermodynamic models. Computer simulation, on the other hand, allows us, for a given intermolecular force model, to test the validity of various molecular-level assumptions, for example, local composition effects in mixtures or the temperature and density dependence of configurational energies or coordination numbers in pure fluids. Thus our work really consists of two parts. First is Monte Carlo computer simulation, and second is the use of these simulation results in a theoretical framework to make broad, generalized statements based on these simulations.

In previous papers (references 1–8) we have considered the derivation of the generalized van der Waals partition function and its application to pure fluids and mixtures of square-well molecules. Our interest here, however, is with molecular force models that are continuous and have long-range tails which therefore mimic the behavior of real molecules. For this reason we use here, as a prototype, the modified

Buckingham exponential-6 potential (ref. 9)

$$u(r) \equiv \begin{cases} \dfrac{\varepsilon}{1-6/\alpha_E}\left[\dfrac{6}{\alpha_E}\exp\left(\alpha_E\left[1-\dfrac{r}{r_m}\right]\right)-\left(\dfrac{r_m}{r}\right)^6\right], & \text{for } r < r_{max} \\ \infty & \text{for } r < r_{max} \end{cases} \tag{1}$$

This potential, which has a hard core, contains 3 parameters ε, σ and α_E characteristic of each molecular species. With this potential model, r_{max} is the smallest positive value of r at which $du(r)/dr = 0$, r_m is the value of the radial separation distance r at which the potential is a minimum and σ represents the point at which $u(r) = 0$, found by setting the term in the outer brackets above equal to zero.

The development of the generalized van der Waals partition function Q for this potential is unchanged from that reported in Reference 1, so that we have for N molecules in volume V at temperature T

$$Q(N, V, T) = \frac{1}{N!}\left(\frac{q_r q_v q_e}{\Lambda^3}\right)^N V_f^N(N, V)\exp\left(\frac{-N\Phi(N, V, T)}{2kT}\right), \tag{2}$$

where $\Lambda = \sqrt{h^2/2\pi mkT}$ is the de Broglie wavelength, h is Planck's constant and m is molecular mass. Note that for small molecules the partition functions for rotation and vibration, q_r and q_v, are functions only of temperature; while for long chain molecules both of these may also be functions of density. The electronic partition function, q_e, is a function only of temperature for nonionized species. In addition, V_f is the free volume of the system, that is, the volume of the system which is accessible to each molecule. The mean potential, Φ, is given by:

$$\Phi(N, V, T) \equiv \frac{-2kT}{N}\int_{T=\infty}^{T}\frac{E^{CONF}(N, V, T)}{kT^2}\,dT \tag{3a}$$

or

$$= \frac{2T}{N}\int_{1/T=0}^{1/T} E^{CONF}(N, V, T)d\frac{1}{T} \tag{3b}$$

where E^{CONF}, the configurational energy of the system, that is, the difference between the real fluid and the ideal gas internal energies. Finally, the configurational energy can be computed from

$$E^{CONF} \equiv \frac{N^2}{2V}\int_v u(\mathbf{r})g(N, V, T; \mathbf{r})\,d\mathbf{r} \tag{4}$$

where the radial distribution function, $g(N, V, T; \mathbf{r})$, is proportional to the probability of finding a molecular center in a volume element at a distance $\mathbf{r}$ from a central molecule at temperature T and number density $\varrho \equiv N/V$. Since only spherical molecules are considered here, the integral over the volume element $d\mathbf{r}$ reduces to $4\pi r^2\,dr$, where r is the radial distance.

For the square-well potential we have (ref. 2)

$$u(r)_{sq} = \begin{cases} \infty, & \text{for } r < \sigma \\ -\varepsilon, & \text{for } \sigma \leqslant r \leqslant R\sigma \\ 0, & \text{for } R\sigma < r \end{cases} \tag{5}$$

and

$$E_{sq}^{CONF} = \frac{N^2}{2V}(-\varepsilon)\int_{\sigma}^{R\sigma} g(N, V, T; r)4\pi r^2 dr \tag{6a}$$

$$= -\frac{\varepsilon}{2} NN_c(N, V, T) \tag{6b}$$

where

$$N_c(N/V, T) \equiv 4\pi\varrho \int_{\sigma}^{R\sigma} g(N, V, T; r)r^2 dr \tag{7}$$

is the temperature and density dependent average number of molecules within the well of a central molecule.

As a result of Eqn. (7), our interest in the square-well fluid was mainly with the coordination number for the pure fluids (ref. 2) and with local composition ratios for mixtures (ref. 3 and 4). For continuously varying potentials, such as the modified Buckingham potential, coordination numbers or local composition ratios contain little information, and, in fact, can only be defined through the introduction of arbitrarily chosen cut-off distances. Consequently, for continuously varying potentials our interest is solely with the unambigously defined configurational energy (Eqn. (4)) and mean potential (Eqn. (3)).

2 SIMULATION RESULTS

The Monte Carlo program of our earlier work was used to compute the configurational energy and, in some cases, the compressibility of the modified Buckingham Exp-6 potential over a wide range of temperature and densities (see Appendix for methodology). The results are given in Tables 1A, B and 2. Some of the results for the configurational energy are plotted in Figure 1a for the high temperature region, and in Figure 1b for the low temperature region. Note that at infinite temperature we can assume that the radial distribution function is zero when molecules overlap (i.e., $r < r_{max}$) and unity elsewhere. In this case

$$E^{CONF}(N, V, T \to \infty) = \frac{2\pi N^2}{V}\left[\int_0^{r_{max}} u(r)\cdot 0 r^2 dr + \int_{r_{max}}^{\infty} u(r)\cdot 1 r^2 dr\right] \tag{8}$$

$$= \frac{2\pi N^2}{V}\frac{\varepsilon}{1 - \frac{6}{\alpha_E}}\int_{r_{max}}^{\infty}\left[\frac{6}{\alpha_E}\exp\left(\alpha_E\left[1 - \frac{r}{r_m}\right]\right) - \left(\frac{r_m}{r}\right)^6\right]r^2 dr \tag{9}$$

$$= \frac{2\pi N^2 r_{max}^3 \varepsilon}{V(1 - \frac{6}{\alpha_E})}\left\{\frac{6}{\alpha_E}\exp\left(\frac{\alpha_E\psi - 1}{\psi}\right)\left[\psi^3 + \psi\left(1 + \psi\right)^2\right] - \frac{(\alpha_E\psi)^6}{3}\right\} \tag{10}$$

where $\psi \equiv r_m/\alpha_E r_{max}$. This equation was used to calculate the configurational energies at the $T \to \infty (\varepsilon/kT \to 0)$ limit in the tables.

Figure 1b also contains the configurational energy for the square-well fluid that we have reported earlier. While the configurational energies for square-well and Buckingham potentials are similar at low temperature (large values of ε/kT), they are marked-

Table 1A Configurational Energies for Exp-6 Fluid from Monte Carlo Simulation†

ε/kT	ϱ^* 0.10	0.25	0.50	0.75	1.00	1.25
$0.0000 \times 10^{+0}$	207.519	518.797	1037.594	1556.391	2075.188	2593.985
0.4107×10^{-3}	32.221	81.607	170.008	268.424	372.740	486.284
0.6160×10^{-3}	23.534	60.817	127.505	203.849	283.944	375.330
0.1232×10^{-2}	13.645	35.634	76.729	124.706	177.650	239.232
0.3080×10^{-2}	6.301	16.988	37.593	62.713	93.779	130.091
0.4107×10^{-2}	4.829	13.239	29.807	50.255	75.875	107.238
0.6160×10^{-2}	3.287	8.980	20.878	36.235	55.942	81.151
0.1232×10^{-1}	1.551	4.412	10.729	19.852	32.364	49.560
0.2464×10^{-1}	0.561	1.707	4.721	9.704	17.496	29.303
0.3080×10^{-1}	0.344	1.095	3.363	7.353	14.034	24.396
0.4107×10^{-1}	0.124	0.495	1.895	4.827	10.203	19.119
0.6160×10^{-1}	−0.110	−0.161	0.351	2.049	5.966	12.943
0.1232	−0.364	−0.852	−1.402	−1.148	0.773	5.454
0.1369	−0.388	−0.923	−1.564	−1.498	0.194	4.561
0.1540	−0.418	−1.002	−1.764	−1.854	−0.460	3.628
0.1760	−0.446	−1.084	−1.979	−2.270	−1.103	2.626
0.2053	−0.474	−1.161	−2.184	−2.662	−1.801	1.565
0.2240	−0.489	−1.206	−2.286	−2.872	−2.181	1.064
0.2464	−0.507	−1.246	−2.389	3.088	−2.549	0.474
0.2738	−0.525	−1.295	−2.495	−3.306	2.960	−0.112
0.3080	−0.544	−1.341	−2.614	−3.522	−3.320	0.751
0.3520	−0.567	−1.396	−2.729	−3.765	−3.741	−2.207
0.4107	−0.592	−1.452	−2.848	−4.010	−4.199	−2.777
0.4928	−0.625	−1.561	−2.973	−4.279	−4.694	−3.504
0.6160	−0.674	−1.615	−3.109	−4.555	−5.227	−4.029
0.8213	−0.778	−1.826	−3.290	−4.848	−5.791	−4.370
1.2320	−1.867	−2.781	−3.676	−5.175	−6.436	−5.415

†Configurational energies expressed in $E^{CONF}/N\varepsilon$. Except for the $\varepsilon/kT = 0$ entries, the results above were obtained using 1.3×10^6 configurations for a 108 molecule system with $r_L \equiv 14.0(\varrho^* \equiv N/V\sigma^3)$.

ly different at high temperatures where the short-range force, and therefore the soft repulsive force of the Buckingham potential, results in a large positive configurational energy. Thus the configurational energy models for the square-well fluid reported earlier will not apply here. Figure 2 also shows the configurational energy for the modified Buckingham potential, but now plotted as a function of density along various isotherms.

Of direct interest for thermodynamic modelling is the mean potential of Eqns. (3). The values of the mean potential found by numerically integrating E^{CONF}/kT using a second-order polynomial quadrature method appear in Table 3, and in Figures 3 and 4 as a function of reduced inverse temperature and reduced density, respectively. Note that the mean potential first increases with decreasing temperature (increasing ε/kT) and then decreases. Also the mean potential increases with increasing density at high temperatures (low ε/kT), but first decreases and then increases with increasing density at low temperatures (high ε/kT).

3 MODELLING THE MEAN POTENTIAL

The mean potential model proposed earlier by Lee and co-workers (ref. 2) is

Table 1B Configurational Energies for Exp-6 Fluid from Monte Carlo Simulation

ε/kT	ϱ^* 0.60	0.70
$0.0000 \times 10^{+0}$	1245.113	1452.632
0.4107×10^{-3}	208.597	248.264
0.6160×10^{-3}	157.309	187.482
0.1232×10^{-2}	95.354	114.192
0.2464×10^{-2}	–	68.388
0.3080×10^{-2}	47.239	57.501
0.4107×10^{-2}	37.342	45.821
0.6160×10^{-2}	26.507	32.879
0.1232×10^{-1}	13.991	17.741
0.2464×10^{-1}	6.448	8.497
0.3080×10^{-1}	4.722	6.378
0.4107×10^{-1}	2.862	4.127
0.6160×10^{-1}	0.857	1.583
0.1232	−1.415	−1.279
0.1369	−1.669	−1.606
0.1540	−1.933	−1.933
0.1760	−2.188	−2.289
0.1895	–	−2.469
0.2053	−2.465	−2.637
0.2200		−2.788
0.2244	−2.608	–
0.2369	–	−2.937
0.2464	−2.758	−3.021
0.2678	–	−3.168
0.2738	−2.898	–
0.2933	–	−3.327
0.3080	−3.054	−3.412
0.3422	–	−3.571
0.2530	−3.210	–
0.3850	–	−3.746
0.4107	−3.372	−3.834
0.4738	–	−4.010
0.4928	−3.540	–
0.5600	–	−4.196
0.6160	−3.716	−4.292
0.6844	−3.790	−4.399
0.7700	−3.872	−4.505
0.8213	−3.917	−4.552
0.8800	−3.957	−4.604
1.0267	−4.051	−4.716
1.2320	−4.174	−4.833

$$\frac{\Phi}{2kT} = -Z_M \ln\left[1 + \frac{\varrho^*}{\sqrt{2}}\left(e^{\varepsilon/2kT} - 1\right)\right], \tag{11}$$

where Z_M is maximum coordination number dependent only on the width of square-well. The mean potential corresponding to the Peng-Robinson equation of state (ref. 10) is

$$\frac{\Phi}{2kT} = \frac{a(T)}{bRT2\sqrt{2}} \ln\left[\frac{1 + b(1 - \sqrt{2})\varrho}{1 + b(1 + \sqrt{2})\varrho}\right], \tag{12}$$

where a and b are equation of state parameters, the former being temperature

Table 2 Compressibilities for Exp-6 Fluid from Monte Carlo Simulation

a/kT	ϱ^* 0.60	0.70
$0.0000 \times 10^{+0}$	1.0000	1.0000
0.4107×10^{-3}	1.2004	1.2380
0.6160×10^{-3}	1.2421	1.2879
0.1232×10^{-2}	1.3280	1.3915
0.2464×10^{-2}	–	1.5253
0.3080×10^{-2}	1.4740	1.5744
0.4107×10^{-2}	1.5280	1.6439
0.6160×10^{-2}	1.6120	1.7531
0.1232×10^{-1}	1.7800	1.9717
0.2464×10^{-1}	1.9700	2.2283
0.3080×10^{-1}	2.0330	2.3177
0.4107×10^{-1}	2.1090	2.4376
0.6160×10^{-1}	2.2110	2.5910
0.1232	2.3140	2.8138
0.1369	2.3140	2.8303
0.1540	2.3060	2.8480
0.1760	2.2970	2.8464
0.1895	–	2.8422
0.2053	2.2610	2.8455
0.2200	–	2.8310
0.2240	2.2270	–
0.2369	–	2.8160
0.2464	2.1830	2.7932
0.2678	–	2.7723
0.2738	2.1400	–
0.2933	–	2.7273
0.3080	2.0470	2.6924
0.3422	–	2.6229
0.3520	1.9410	–
0.3850	–	2.5036
0.4107	1.7680	2.4294
0.4738	–	2.2399
0.4928	1.5150	–
0.5600	–	1.9501
0.6160	1.0960	1.7645
0.6844	0.8504	1.4636
0.7700	0.5077	1.0741
0.8213	0.3250	0.8719
0.8800	0.1039	0.6429
1.0267	−0.4912	−0.0411
1.2320	−1.2870	−0.9488

dependent. Similarly the mean potential equation corresponding to the Redlich-Kwong equation of state (ref. 11) is

$$\frac{\Phi}{2kT} = -\frac{a}{\sqrt{T}bRT} \ln [1 + b\varrho], \tag{13}$$

Clearly all of these models result in a mean potential which is monotonically decreasing with increasing density, unlike our simulation results which first decrease and then increase with density a moderate temperatures. Thus one method of modelling the mean potential data would be to use models with more complicated density dependence, resulting in complicated equations of state. Another procedure, and the

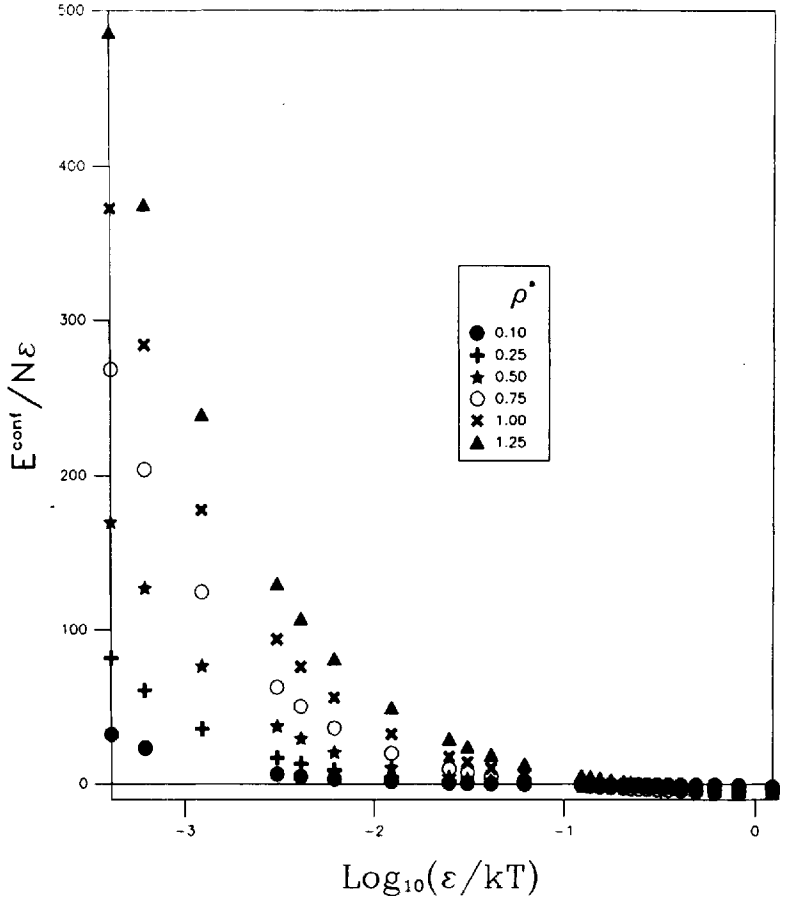

Figure 1a Configurational energy for the Exp-6 fluid from Monte Carlo simulations on a 108-molecule system.

one followed here is to, instead, consider a redefinition of the free volume and mean potential terms.

The mean potential appears in the generalized van der Waals partition function only in the product

$$V_f \exp\left(-\frac{\Phi}{2kT}\right) \tag{14}$$

For the square-well fluid the free volume V_f contains only contributions from the central hard-core, while the mean potential results from the attractive well. For the modified Buckingham and other continuous potentials one could consider the free volume to result only from the hard core of the potential, and Φ to result from all potential contributions for $r > r_{max}$. This is what has been done above. Another alternative is to identify an effective hard core diameter d_{HS} at each temperature and use this in the free volume term (which we denote by V_f^*). The mean potential in this case Φ^* is computed from

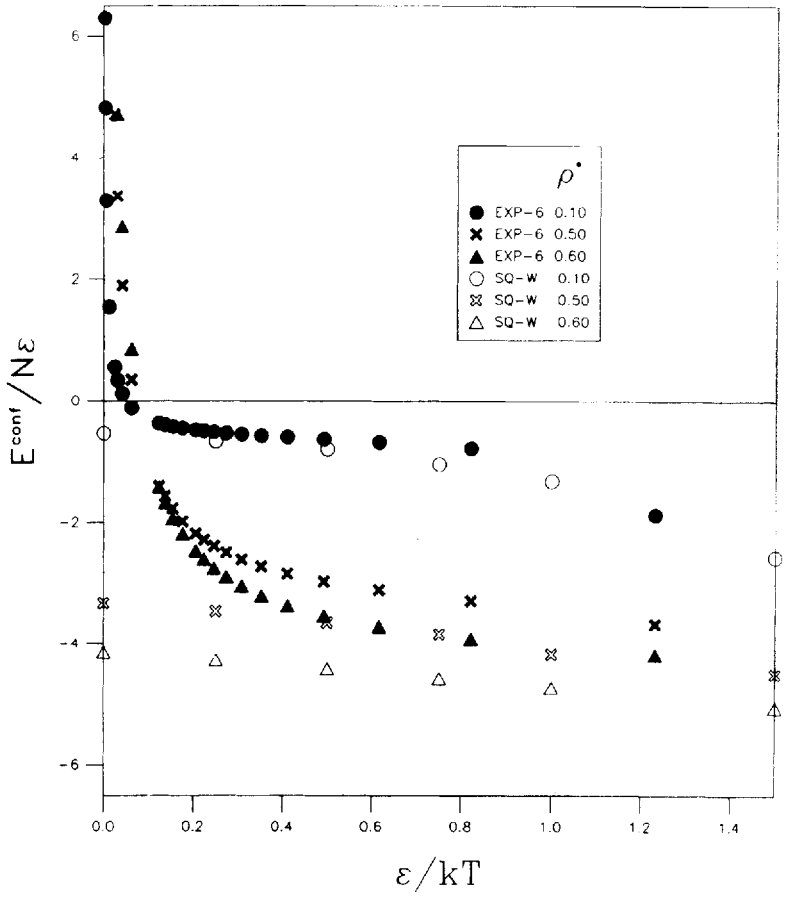

Figure 1b Configurational energy for the Exp-6 and square-well fluids from Monte Carlo simulations.

$$\Phi^* = \Phi - 2kT \ln \frac{V_f}{V_f^*} \tag{15}$$

where Φ is the mean potential in Tables 3A, B, and V_f and V_f^* are the free volumes computed for hard-core fluids of diameters r_{max} and d_{HS}, respectively.

For the calculations here we have used the free volume term derived from the Kim-Lin-Chao representation of the hard sphere fluid (ref. 12)

$$V_f = V\left(1 - 0.42N \frac{b}{N_a V}\right)^{17.6} \tag{16}$$

where $b = 2\pi d_{HS}^3/3$ and N_a is Avogadro's number. The Barker and Henderson theory (ref. 13) provides a simple way of defining a reasonably accurate hard-core diameter from

$$d_{HS}(T) = \int_0^\sigma \{1 - \exp[-\beta u(r)]\} dr, \tag{17}$$

where $\beta = 1/kT$ and σ is the radial distance at which the potential equals zero. Figure 5

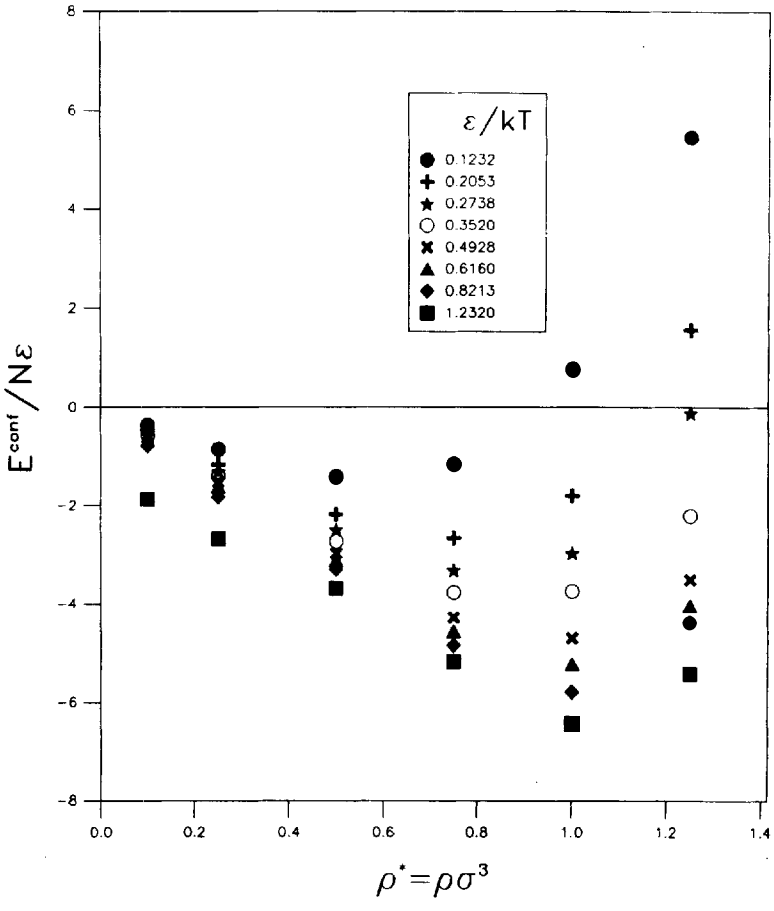

Figure 2 Configurational energy for the Exp-6 fluid from Monte Carlo simulation on a 108-molecule system.

contains the results for the quantity

$$\Delta = (d_{HS} - r_{max})/r_m \tag{18}$$

The solid line represents the results from the integral of Eqn. (17). Note that at high temperatures $\Delta \to 0$ while at low temperatures $\Delta \to (\sigma - r_{max})/r_m$. The values of Δ were fit with an average percent error of 1.3% for the range of ε/kT from 0 to 3 and α_E from 11 to 22 with the function

$$\Delta = \frac{\zeta\sqrt{\varepsilon/kT}}{\eta + \sqrt{\varepsilon/kT}}. \tag{19}$$

where

$$\zeta = (\sigma - r_{max})/r_m \tag{20}$$

Table 3A Mean Potential Data for the Exp-6 Fluid from Numerical Integration†

ε/kT	ϱ^*					
	0.10	*0.25*	*0.50*	*0.75*	*1.00*	*1.25*
$0.0000 \times 10^{+0}$	0.000	0.000	0.000	0.000	0.000	0.000
0.6160×10^{-3}	0.047	0.118	0.238	0.364	0.492	0.624
0.1232×10^{-2}	0.057	0.146	0.297	0.459	0.626	0.803
0.3080×10^{-2}	0.071	0.182	0.379	0.596	0.827	1.082
0.4107×10^{-2}	0.079	0.203	0.424	0.669	0.935	1.229
0.6160×10^{-2}	0.087	0.225	0.475	0.755	1.067	1.419
0.1232×10^{-1}	0.100	0.260	0.560	0.909	1.313	1.787
0.2464×10^{-1}	0.110	0.292	0.640	1.068	1.587	2.229
0.3080×10^{-1}	0.114	0.303	0.672	1.132	1.699	2.414
0.4107×10^{-1}	0.117	0.311	0.699	1.193	1.822	2.635
0.6160×10^{-1}	0.116	0.313	0.719	1.259	1.981	2.955
0.1232	0.098	0.273	0.665	1.249	2.133	3.440
0.1369	0.094	0.264	0.652	1.244	2.157	3.537
0.1540	0.088	0.248	0.623	1.215	2.155	3.606
0.1760	0.078	0.225	0.582	1.169	2.139	3.675
0.2053	0.064	0.192	0.521	1.097	2.095	3.736
0.2240	0.055	0.170	0.479	1.045	2.058	3.760
0.2464	0.044	0.142	0.427	0.978	2.005	3.778
0.2738	0.030	0.107	0.360	0.891	1.930	3.782
0.3080	0.012	0.062	0.272	0.774	1.822	3.767
0.3520	−0.013	0.002	0.155	0.613	1.666	3.706
0.4107	−0.047	−0.082	−0.009	0.385	1.433	3.549
0.4928	0.097	−0.204	−0.248	0.044	1.066	3.294
0.6160	−0.177	−0.397	−0.624	0.502	0.453	2.822
0.8213	−0.325	−0.746	−1.282	−1.469	−0.687	1.951
1.2320	−0.826	−1.649	−2.702	−3.533	−3.211	−0.035

† Mean Potential data expressed as $\Phi/2kT$.

and

$$\eta = 1/[-56.74580 + 8.6247\alpha_E - 0.30349\alpha_E^2 + 0.0048416\alpha_E^3] \tag{21}$$

This equation is shown as the dashed line in Fig. 5 for the case of $\alpha_E = 14.0$. Thus, we have

$$V_f = V\left(1 - 0.42\frac{N}{V}\left[\frac{2\pi}{3}\left(r_{max} + \Delta(T)r_m\right)^3\right]\right)^{17/6} \tag{22}$$

and

$$\Phi^* = \Phi - 2kT\frac{17}{6}\ln\left[\frac{1 - 0.42\varrho^*\left[\frac{2\pi}{3}\left(\frac{r_{max}}{\sigma}\right)^3\right]}{1 - 0.42\varrho^*\left[\frac{2\pi}{3}\left(\frac{r_{max} + \Delta(T)r_m}{\sigma}\right)^3\right]}\right] \tag{23}$$

The values of Φ^* as a function of ε/kT and ϱ^* are given in Fig. 6. The most important observation from this table and figure is that the mean potential Φ^* is monotonically

Table 3B Mean Potential Data for the Exp-6 Fluid from Numerical Integration

ε/kT	ϱ^*	
	0.60	*0.70*
$0.0000 \times 10^{+0}$	0.000	0.000
0.6160×10^{-3}	0.288	0.338
0.1232×10^{-2}	0.361	0.426
0.2464×10^{-2}	–	0.528
0.3080×10^{-2}	0.464	0.571
0.4107×10^{-2}	0.520	0.624
0.6160×10^{-2}	0.583	0.703
0.1232×10^{-1}	0.694	0.841
0.2464×10^{-1}	0.802	0.981
0.3080×10^{-1}	0.845	1.037
0.4107×10^{-1}	0.883	1.090
0.6160×10^{-1}	0.917	1.145
0.1232	0.873	1.119
0.1369	0.861	1.111
0.1540	0.830	1.081
0.1760	0.785	1.034
0.1895	–	1.002
0.2053	0.716	0.962
0.2200	–	0.922
0.2240	0.669	–
0.2369	–	0.874
0.2464	0.609	0.845
0.2678	–	0.779
0.2738	0.531	–
0.2933	–	0.696
0.3080	0.429	0.647
0.3422	–	0.527
0.3520	0.291	–
0.3850	–	0.371
0.4107	0.098	0.273
0.4738	–	0.025
0.4928	−0.186	–
0.5600	–	−0.329
0.6160	−0.634	−0.566
0.6844	−0.891	−0.864
0.7700	−1.219	−1.245
0.8213	−1.418	−1.477
0.8800	−1.649	−1.746
1.0270	−2.237	−2.430
1.2320	−3.081	–

decreasing with density as was the case for the square-well fluid and each of the models considered earlier (Eqns. 11, 12 and 13).

In fact, with this theoretically correct redefinition of the contribution to the free volume and mean potential, we find that the latter can be represented by

$$\frac{\Phi(N, V, T)}{2kT} = \alpha(\varepsilon/kT)\varrho^*. \tag{24}$$

Further using

$$\alpha(\varepsilon/kT) = c_1 \frac{\varepsilon}{kT} + c_2 \left[\sqrt{\frac{\varepsilon}{kT}} - \frac{\varepsilon}{kT}\right], \tag{25}$$

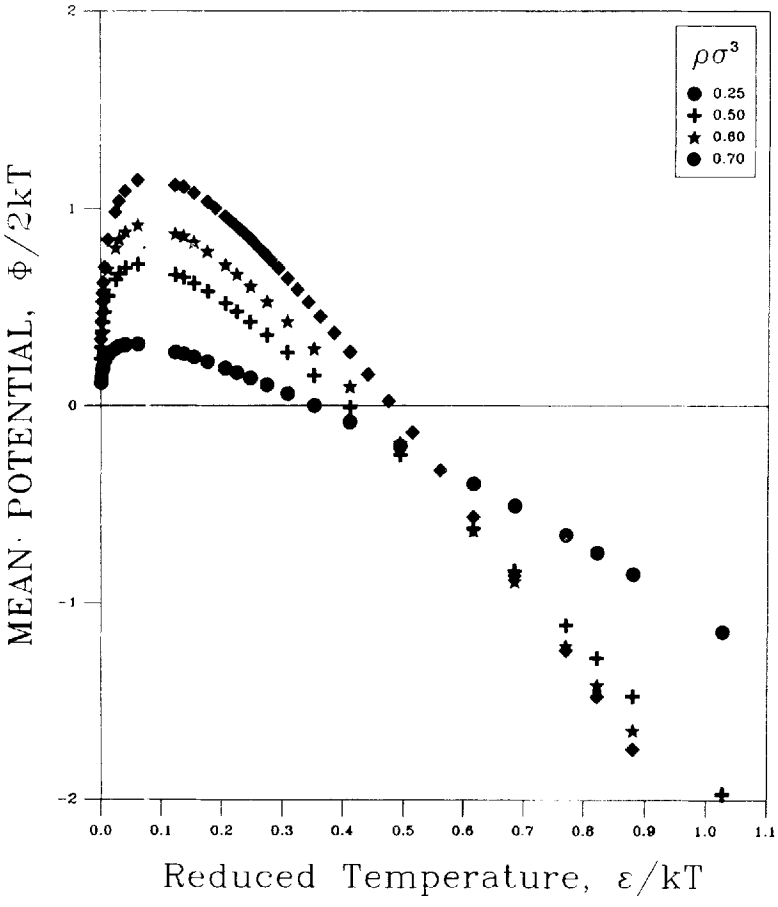

Figure 3 Temperature depedence of the mean potential of Exp-6 fluid.

with $c_1 = -6.23343$ and $c_2 = 0.206317$ produces an average error of 4% in the mean potential over the range of conditions $kT/\varepsilon = 0.9$ to 9.9 and $\varrho^* = 0.1$ to 1.25.

4 A SIMPLE EQUATION OF STATE FOR THE MODIFIED BUCKINGHAM EXPONENTIAL-6 POTENTIAL

With the results of the previous section and the relationships between the canonical partition function and thermodynamic properties

$$A(N, V, T) = -kT \ln Q(N, V, T) \tag{26}$$

$$P(N, V, T) = kT\left(\frac{\partial \ln Q(N, V, T)}{\partial V}\right)_{N,T} \tag{27}$$

we can now write both the fundamental equation of state $A = A(N, V, T)$ and the

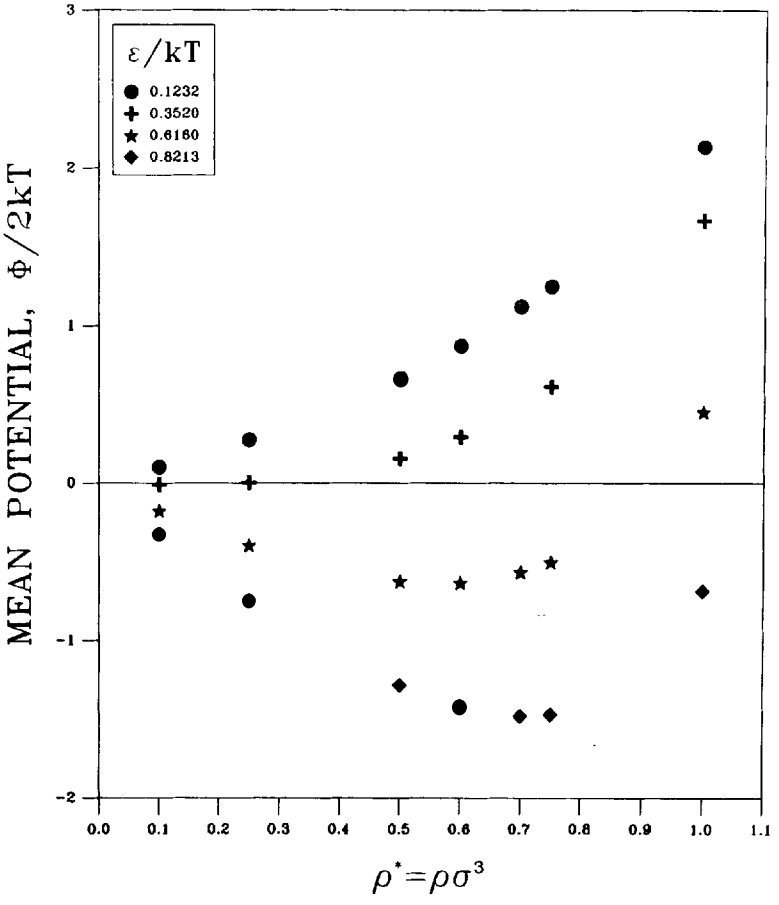

Figure 4 Density dependence of the mean potential of Exp-6 fluid.

volumetric equation of state $P = P(N, V, T)$ of a fluid composed of modified Buckingham exponential-6 molecules. In particular, the volumetric equation of state is

$$P = \frac{RT\,(v + 0.77b(T))}{v\,(v - 0.42b(T))} - \frac{RT}{v}\frac{a(T)}{v}, \tag{28}$$

where v is the molar volume, R is the gas constant, $\alpha(T) \equiv -\alpha(\varepsilon/kT)\sigma^3 N_a$ and $b(T)$ is given by

$$b(T) = \frac{2\pi}{3}\left(\frac{r_{max} + \Delta(T)r_m}{\sigma}\right)^3 \sigma^3 N_a \tag{29}$$

The equation leads to an average absolute deviation in the compressibility of 0.6 over the range of kT/ε from 1.1 to ∞, and range of reduced density $\varrho\sigma^3$ from 0 to 0.75.

With this simple, yet reasonably accurate equation of state we can estimate other properties of Buckingham fluid. For example, using the conditions that

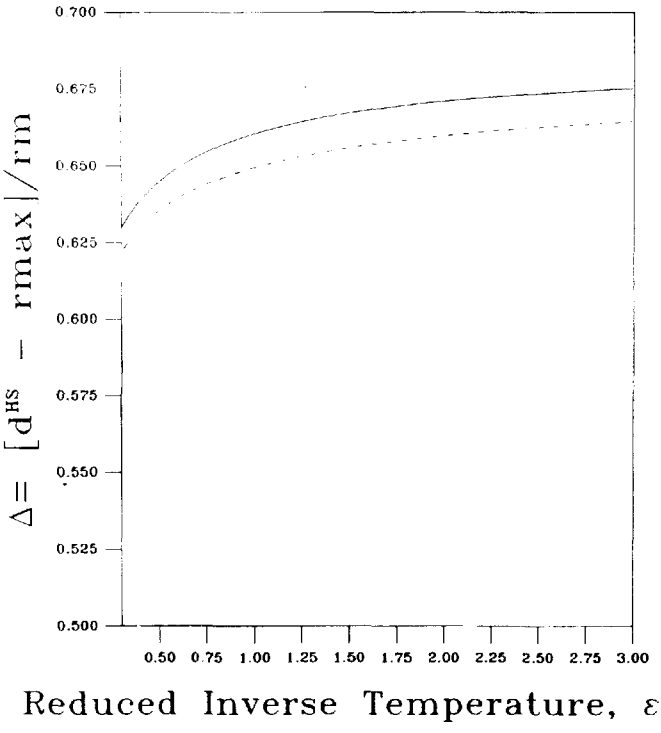

Figure 5 Effective hard-core diameter for Exp-6 having $\alpha_E = 14$.

$$\left(\frac{\partial P}{\partial v}\right)_{T=T_c} = \left(\frac{\partial^2 P}{\partial v^2}\right)_{T=T_c} = 0 \tag{30}$$

we obtain the results in Table 4 for the reduced critical temperature, critical pressure and critical compressibility as a function of the parameter α_E. Similarly, from the equality of fugacities in the vapor and liquid phases, we obtain the vapor-pressure of the Buckingham fluid as a function of reduced temperature and the parameter α_E given in Fig. 7. Finally, it is of interest to compute the acentric factor ω of Pitzer defined as (ref. 14)

$$\omega = -1.0 - \log_{10}\left(\frac{P^{vap}(T_r = 0.7)}{P_c}\right) \tag{31}$$

for the modified Buckingham exponential-6 fluid. These also appear in the Table 4.

5 CONCLUSIONS

In this paper we report extensive canonical ensemble Monte Carlo simulation results for a fluid composed of Buckingham modified exponential-six molecules. The data for the configurational energy cover a wide range of temperature and density; some results for the compressibility are also reported. The configurational energy data were

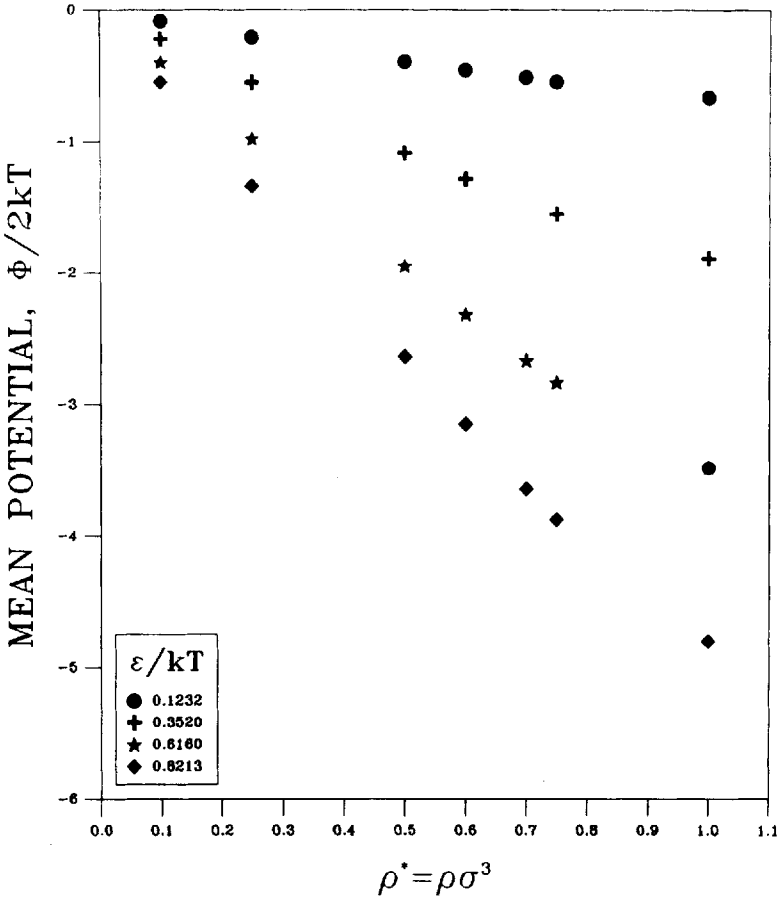

Figure 6 Density dependence of a new mean potential.

interpreted using the generalized van der Waals partition function proposed earlier. Indeed, it is this partition function that allows us to make the bridge from our simulation data to general macroscopic thermodynamic models. However, it is only on the basis of the simulation results that reasonable assumptions could be identified for use in this partition function.

Though, at first, the simulation data appear to suggest a complicated dependence of the configurational energy and mean potential on temperature and density for this continuous potential, we find that by a judicious definition of the free volume using the Barker-Henderson effective hard-sphere diameter, the mean potential is a linear function of density and a simple function of temperature. As a result, we find that the exponential-six fluid can be described by a van der Waals-like equation of state with a and b parameters having well-defined, theoretically-based temperature dependencies.

Using this equation of state description, we then completely characterized the exponential-six fluid by calculating the critical properties and acentric factor as a function if its potential parameters, and its binodal curve as a function of tem-

Table 4 Critical Constants of Buckingham Exponential-6 Fluid

α_i	kT_c/ε	$P_c\sigma^3/\varepsilon$	ω
11.	1.3874	0.1712	−0.1069
12.	1.3265	0.1563	−0.0940
13.	1.2923	0.1483	−0.0858
14.	1.2696	0.1431	−0.0800
15.	1.2532	0.1394	−0.0756
16.	1.2405	0.1366	−0.0721
17.	1.2303	0.1343	−0.0692
18.	1.2217	0.1324	−0.0668
19.	1.2144	0.1308	−0.0646
20.	1.2080	0.1294	−0.0627
21.	1.2023	0.1282	−0.0610
22.	1.1971	0.1271	−0.0595
23.	1.1922	0.1260	−0.0580
24.	1.1877	0.1251	−0.0566
25.	1.1834	0.1242	−0.0553
26.	1.1793	0.1233	−0.0540
27.	1.1754	0.1225	−0.0528
28.	1.1716	0.1217	−0.0516
29.	1.1680	0.1209	−0.0505
30.	1.1645	0.1202	−0.0494

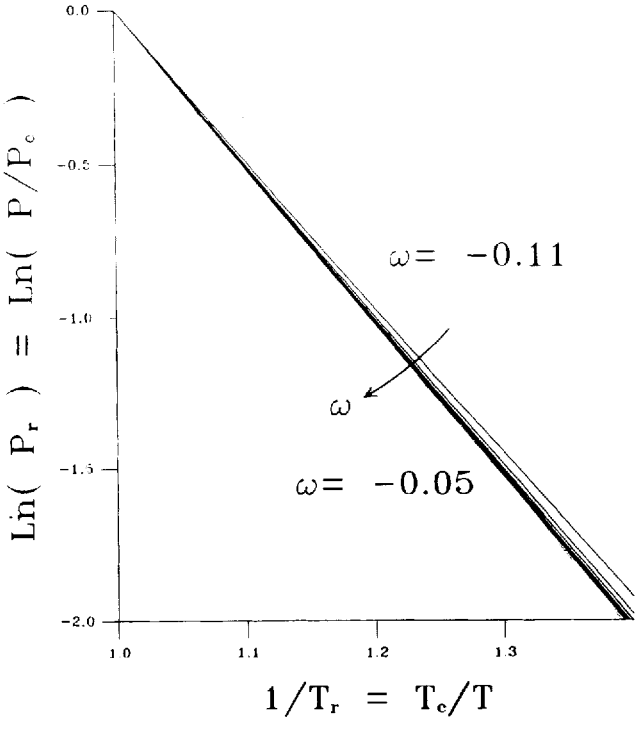

Figure 7 Vapor pressure of Exp-6 fluid.

perature. In addition to the specific calculations reported here for the exponential-six fluid, an important contribution of this paper is to show how fluids represented by continuous potential functions can be studied using the generalized van der Waals partition function. In particular, we establish that though there appears to be some degree of arbitrariness in separating the partition function into the free volume and mean potential terms when using a continuous potential, if a theoretically-based hard core diameter is used in the free volume term there is no ambiguity, and the resulting description is relatively simple.

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References

[1] S.I. Sandler, "The generalized van der Waals partition function. I. Basic theory," *Fluid Phase Equilibria,* **19,** 233–257 (1985).
[2] K.-H. Lee, M. Lombardo and S.I. Sandler, "The generalized van der Waals partition function. II. Application to the square-well fluid." *Fluid Phase Equilibria,* **21,** 177–196 (1985).
[3] K.-H. Lee, S.I. Sandler and N.C. Patel, "The generalized van der Waals partition function. III. Local composition models for a mixture of equal size square-well molecules," *Fluid Phase Equilibria,* **25,** 31–49 (1986).
[4] K.-H. Lee and S.I. Sandler, "The generalized van der Waals partition function. IV. Local composition models for a mixture of unequal size molecules," *Fluid Phase Equilibria,* **34,** 113–147 (1987).
[5] K.-H. Lee, S.I. Sandler and P.A. Monson, "Local compositions and the square well fluid," *Intl. J. Thermodyn.* **7,** 367–379 (1986).
[6] S.I. Sandler, K.-H. Lee and H. Kim, "The generalized van der Waals partition function as a basis for equations of state, their mixing rules and activity coefficient models," *ACS Symp. Ser,* **300,** Washington, D.C. (1986).
[7] S.I. Sandler and K.-H. Lee, "A proper theorectical basis for local composition mixing rules and a new class of activity coefficient models," *Fluid Phase Equilibria* **30,** 135–142 (1986).
[8] S.I. Sandler and J.M. Prausnitz, "Molecular thermodynamics for chemical process design: Applications of generalized van der Waals theory," *Proceedings of the Joint CIESC-AIChE Meeting* (Beijing, China, Sept. 1982) **1,** 49–59 (1982).
[9] R.A. Buckingham, "The classical equation of state of gaseous helium, neon and argon," *Proc. Roy. Soc.* **168A,** 264–283 (1938).
[10] D.Y. Peng and D.B. Robinson, "A New Two-Constant Equation of State," *Ind. Eng. Chem. Fundam.,* **15,** 59–64 (1976).
[11] O. Redlich and J.N.S. Kwong, "On the Thermodynamics of Solutions. V. An Equation of State," *Chem. Rev.,* **44,** 233–244 (1949).
[12] H. Kim, H.M. Lin, and K.C. Chao, "Cubic Chain-of-Rotators Equation of State," *Ind. Eng. Chem.,* **25,** 75–84 (1986).
[13] J.A. Barker and D. Henderson, "Perturbation theory and equation of state for fluids. II. A successful theory of liquids," *J. Chem. Phys.,* **47,** 4714–4721 (1967).
[14] K.S. Pitzer, "Origin of the Acentric Factor," *ACS Symp. Ser.,* **60,** (1977).
[15] M. Lombardo, Master's dissertation: "Monte Carlo Simulation of Liquid Ethane and Propane," University of Delaware (1981).
[16] J.M. Hammersley and D.C. Handscomb, *Monte Carlo Methods,* Wiley, New York (1964).
[17] J.O. Hilschfelder, C.F. Curtiss and R.B. Bird, *Molecular Theory of Gases and Liquids,* Wiley, New York (1964).
[18] N. Metropolis, A.W. Rosenbluth, M.N. Rosenbluth, A.H. Teller and E. Teller, "Equation of state calculations by fast computing machines," *J. Chem. Phys.,* **21,** 1087–1092 (1953).

APPENDIX

A Monte Carlo program (ref. 15) was altered to calculate the configurational energy and radial distribution function for the Exp-6 potential. The following parameters for the Exp-6 potential for argon were used in the program (ref. 16):

$$\begin{aligned} \varepsilon/k &\equiv 123.2\,\text{K} \\ r_m &\equiv 3.866\,\text{Å} \\ \alpha_E &\equiv 14.0 \end{aligned} \tag{A.1}$$

The remaining parameters, r_{max}, the radial distance at which ϕ becomes infinite, and σ, the intermolecular diameter, must be determined numerically. The r_{max} parameter is defined such that $[d\phi/dr \mid_{r=r_{max}}] = 0$, and is the smallest positive root of:

$$\left(\frac{r_{max}}{r_m}\right)^7 \exp\left(\alpha_E\left[1 - \frac{r_{max}}{r_m}\right]\right) = 1. \tag{A.2}$$

Finally, $\phi(r) = 0$ when $r = \sigma$ and therefore σ is defined by:

$$\left(\frac{\sigma}{r_m}\right)^6 \exp\left(\alpha_e\left[1 - \frac{\sigma}{r_m}\right]\right) = \frac{\alpha_E}{6}. \tag{A.3}$$

Using Eqs. A.1–A.3, the following values for the remaining parameters were found:

$$\begin{aligned} r_{max} &= 0.7855\,\text{Å} \\ \sigma &= 3.4373\,\text{Å} \end{aligned} \tag{A.4}$$

Simulations were performed using the standard Metropolis technique (refs. 17 and 18) on a cube containing 108 spherical molecules. An initial number of configurations ($1 - 3 \times 10^4$) were generated prior to averaging over $1 - 3 \times 10^6$ configurations.

The program samples 1.1 million configurations for each state point for 108 spherical molecules in 3.13 CPU hours on a VAX 11/785 computer. Additional Monto Carlo work was done on CRAY-X/MP computers at ATT Bell Laboratories and at the Pittsburgh Supercomputer Center. The FORTRAN program developed for the VAX 11/785 ran a similar number of configurations on the CRAY in 13.5 CPU minutes and in 5–8.5 CPU minutes after vectorization.