

A one molecular fluid approximation for diatomic fluid mixtures

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We investigate a one component molecular fluid approximation for conformally similar molecules. We test this scheme on (two) mixtures of rigid homonuclear diatomic Lennard-Jones (LJ) fluids for which a limited amount of information from molecular dynamics simulations is available. For two components of approximately equal bond length but different LJ parameters our results compare favorably with the machine computations. From the very few simulation data available for equimolar mixtures of molecules differing only in their bond lengths we cannot reach any firm conclusion. Alternative procedures for treating general molecular fluid mixtures are discussed.

I. INTRODUCTION

The development of simple accurate approximation schemes for the thermodynamics and structure of dense fluids is a problem of great practical importance and also a theoretical challenge. While the existence of such approximations for fluids in general is by no means *a priori* obvious the results on spherical single component fluids and "some" mixtures¹ strongly suggest the possibility. This motivates the search for similar procedures for nonspherical fluids where the situation is less satisfactory at the present time, although a certain amount of progress has been made in recent years—especially for nonpolar one component diatomics.² It is the purpose of this note to investigate a simple scheme for mixtures of such molecules.

II. FORMULATION OF THE PROBLEM

The interactions in an n -component mixture of symmetric diatomic molecules interacting via site-site pair potentials have the form

$$v_{ij}(\mathbf{R}, \Omega_1, \Omega_2) = \sum_{\pm} \psi_{ij}(|\mathbf{R} \pm 1/2l_i \Omega_1 \pm 1/2l_j \Omega_2|), \quad (1)$$

where \mathbf{R} is the vector between the centers of molecule 1 of species i and molecule 2 of species j , and Ω_k , $k = 1, 2$, is a unit vector along the axis of molecule k . l_i and l_j are the bond lengths of the molecules of species i and j , respectively, and $\psi_{ij}(r)$ is the site-site potential between a site of species i and a site of species j . The summation in Eq. (1) is over all possible $+$, $-$ pairs in the argument of ψ_{ij} .

We shall focus here on the particular case

$$\psi_{ij}(r) = \epsilon_{ij} \Psi_{LJ}(r/\sigma_{ij}), \quad \Psi_{LJ}(y) = 4[y^{-12} - y^{-6}] \quad (2)$$

for which there are now some machine computations available for comparison with theory. One of these computations corresponds to parameter values of this system used for the modeling of CO_2 - C_2H_6 mixture around zero pressure.³ The other corresponds to mixtures of N_2 with molecules having

the same σ and ϵ as N_2 ,⁴ but either half or twice its bond length.⁵ To be specific, l/σ for N_2 denoted in Ref. 5 by N-N is 0.3292 while $l/\sigma = 0.1646$ and $l/\sigma = 0.6584$, respectively, for the molecules denoted in Ref. 5 by N-N and N--N.

We are motivated to investigate this system at the present time by a desire to find the "best" extension of the recently developed sphericalization procedure, the median potential,^{2,6,8,9} to mixtures. The median potential, which has been modified in various ways,⁷ has been found to give good results for single component diatomics with relatively little labor.^{2,6-9} The analysis is particularly simple and accurate for one component LJ molecules where MacGowan⁷ found that the best modified median is obtained by splitting the potential in Eq. (2) into its power law components. This gives a median with a universal dependence on ϵ , σ , and l .

There are various ways that one can imagine generalizing the median prescription to mixtures. One of the simplest is to sphericalize all angle dependent potentials v_{ij} about the centers (or some other suitable points) of each molecule and then use existing theories of spherical fluid mixtures. This is the path followed in Ref. 10 for "hard" mixtures of dumbbells, spherocylinders, and spheres. For the available simulation results on such systems the resulting mixtures of "median" hard spheres turned out to be very nearly additive—for which the Mansoori-Carnahan-Starling-Leland approximation is known to be quite accurate.

For softer interactions there is no simple theory even for spherical mixtures except for the case of van der Waals' type interactions $\phi_{ij}(r) = \epsilon_{ij} \Phi(r/\sigma_{ij})$. For such mixtures the "vdW one-fluid theory" in which a mixture with densities $\rho_i = x_i \rho$ is represented by a one component fluid with density ρ and potential $\bar{\epsilon} \Phi(r/\bar{\sigma})$

$$\bar{\sigma}^3 = \sum x_i x_j \sigma_{ij}^3, \quad (3)$$

$$\bar{\epsilon} = \sum x_i x_j \sigma_{ij}^3 \epsilon_{ij} / \bar{\sigma}^3, \quad (4)$$

is at least as accurate as much more elaborate procedures. This mixing rule has been extended recently by Ree¹¹ to mixtures of particles interacting via exponential-six potentials

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where $\phi_{ij}(r)$ is of the form $\epsilon_{ij}\Phi(r/\sigma_{ij}, \alpha_{ij})$, $\Phi(y, \alpha) = \{6 \exp[\alpha(1-y)] - \alpha/y^6\}/(\alpha - 6)$. It was found there, by trial and error, that adding to Eqs. (3) and (4) the rule

$$\bar{\alpha} = \sum x_i x_j \epsilon_{ij} \sigma_{ij}^3 \alpha_{ij} / (\bar{\epsilon} \bar{\sigma}^3) \quad (5)$$

gave *very good* results over a wide range of densities and temperatures. This is encouraging as it shows again that suitable simple schemes do work.

Unfortunately the spherical potentials $w_{ij}(R)$ obtained by "medianizing" the angle dependent potentials $v_{ij}(R, \Omega_1, \Omega_2)$ are not generally given by a simple formula for which Eqs. (3) and (4) can be used directly. This is true even for the case in Eqs. (1) and (2). It therefore occurred to us that since the site-site potentials in Eq. (2) are of simple form, it is worth trying a molecular one-fluid theory in which $\bar{\sigma}$ and $\bar{\epsilon}$ would still be given by Eqs. (3) and (4), and \bar{l} would be given by a suitable mixing rule. In the present work we exclusively use the simple rule

$$\bar{l} = \sum x_i l_i \quad (6)$$

for the equivalent bond length.

A plausibility argument is given in the Appendix for a more complicated rule (A16) for \bar{l} , similar to Eq. (5), but for all mixtures where simulations are available the \bar{l} 's obtained from Eqs. (6) and (A16) are almost identical (in many cases exactly so). For the computer simulations of the CO₂-C₂H₆ mixture treated as rigid diatomics,³ the two lengths l_1 and l_2 are very close to each other and so any reasonable mixing rule will give essentially the same \bar{l} . For the mixtures of Ref. 5, on the other hand, one is just testing the mixing rule (6) for \bar{l} . Unfortunately the number of available results is not sufficient to permit, at this time, testing of different possibilities for \bar{l} and indeed there appears to be at least one misprint among the published data in Ref. 5. Additional computer simulations systematically varying the parameters ϵ_{ij} , σ_{ij} , l_i , and x_i would be most useful.

III. RESULTS

With the $\bar{\epsilon}$, $\bar{\sigma}$, and \bar{l} given by Eqs. (3), (4), and (6), we sphericalize using MacGowan's procedure⁷ for diatomic Lennard-Jones potentials and use the resulting spherical po-

tential in Ross' semiempirical variational procedure¹² to obtain the Helmholtz free energy, and from it by numerical differentiation the reported pressures. We also calculate the excess internal energy wherever it is available from the simulation. We remark that our calculations are very quick, requiring less than 1 s of CPU time on a DEC 20 computer per thermodynamic point.

We compare the available results of molecular dynamics simulations of CO₂-C₂H₆³ with our calculations in Tables I, II, and III. Since the molecular dynamics calculations for CO₂-C₂H₆ have as one of their purposes to obtain the set of σ_{ij} , ϵ_{ij} , $i, j = 1, 2$, that gives the best intermolecular potential for that system, we see entries in Tables I-III corresponding to different values of those parameters, at a few different thermodynamic points.

Our results for the CO₂-C₂H₆ mixture are promising. The compressibility factors pV/NkT , which are near zero, agree with the molecular dynamics calculations within about 0.2 which corresponds to differences in pressures of about 10 MPa, and the excess internal energies per molecule in units of kT , U/NkT to within 0.2 which corresponds to differences in excess internal energy of about 0.5 kJ/mol. These discrepancies are about a factor of 2 larger for the pressures and about the same for U than those observed when using the median procedure for the pure CO₂ and C₂H₆ fluids. Also the tendencies for our calculated values are the same as for the simulations.

We show in Table IV the comparison between this one-molecular fluid approach plus "medianization" with the results available for pure fluids and mixtures of molecules of elongations l/σ of 0.6584, 0.3292, and 0.1646, respectively.⁵ As already mentioned these molecules are denoted in Ref. 5 by N-N, N-N, and N-N and all have the same ϵ and σ as N₂. The few results available do not allow us to draw any firm conclusion. We believe that the excess internal energy reported in Ref. 5 for the pure N-N fluid is in error (see Table IV).

Our results show that the approach taken could be fruitful. However, more data from computer simulations are needed before one can opt on a firm basis for one of the possible routes to an extension of the vdW-one-fluid approximation now in use for mixtures of spherical molecules to mixtures of nonspherical molecules.

TABLE I. Comparison between the molecular dynamics (MD) calculations (Ref. 3) and the "medianized" one-fluid molecular approximation explained in the text for a mixture of CO₂ (subindex 1)-C₂H₆ treated as rigid Lennard-Jones diatomics with $l_1 = 2.370 \text{ \AA}$ and $l_2 = 2.349 \text{ \AA}$. The compressibility factors are near zero so that small absolute differences are large in relative terms. The temperature was $T = 241 \text{ K}$, $\sigma_{11} = 2.989 \text{ \AA}$, $\epsilon_{11}/k = 163.6 \text{ K}$, $\epsilon_{22}/k = 137.5 \text{ K}$.

Number density $\rho(\text{\AA}^{-3})$	Concentration of CO ₂						Compressibility factor PV/NkT	
	x_1	$\bar{l}(\text{\AA})$	$\sigma_{22}(\text{\AA})$	$\sigma_{12}(\text{\AA})$	$\epsilon_{12}/k(\text{K})$	This work	MD	
0.01082	0.50	2.370*	3.506	3.248	150.0	-0.54	-0.376	
		2.360*				-0.58		
		2.349*				-0.61		
0.01082	0.50	2.360	3.506	3.300	145.0	-0.35	0.024	
0.00865	0.35	2.356	3.550	3.300	145.0	-1.02	-0.647	
0.01037	0.35	2.356	3.550	3.300	145.0	-0.08	0.074	

*These three values are l_1 , $(l_1 + l_2)/2$, and l_2 , respectively. They are included to see how our results in a particular case are altered by varying \bar{l} from l_1 to l_2 .

TABLE II. The same as Table I. $T = 269.3$ K, $\sigma_{11} = 3.035$ Å, $\sigma_{22} = 3.592$ Å, $\sigma_{12} = 3.3135$ Å, $\epsilon_{11}/k = 163.3$ K, $\epsilon_{22}/k = 137.5$ K.

Number density $\rho(\text{Å}^{-3})$	Concentration of CO ₂		ϵ_{12}/k (K)	Compressibility factor PV/NkT		Excess internal energy per molecule in units of kT U/NkT	
	x_1	\bar{l} (Å)		This work	MD	This work	MD
0.008 33	0.00	2.349	149.85	0.02	0.059	- 4.55	- 4.421
0.013 02	1.00	2.370	149.85	- 0.13	0.066	- 5.11	- 5.324
0.010 23	0.70	2.364	149.85	- 0.54	- 0.226	- 4.41	- 4.573
0.010 23	0.70	2.364	120.0	- 0.08	0.099	- 3.98	- 4.149

TABLE III. The same as Table I. $T = 269.25$ K. The Lennard-Jones parameters are $\sigma_{11} = 3.035$ Å, $\sigma_{22} = 3.520$ Å, $\sigma_{12} = 3.2775$ Å, and $\epsilon_{11}/k = 163.29$ K, $\epsilon_{22}/k = 137.49$ K, $\epsilon_{12}/k = 120$ K. The uncertainty in the MD compressibility factors is estimated to be ± 0.01 .

Number density $\rho(\text{Å}^{-3})$	Concentration of CO ₂		\bar{l} (Å)	Compressibility factor PV/NkT		Excess internal energy per molecule in units of kT U/NkT	
	x_1			This work	MD	This work	MD
0.013 69	1		2.370	0.33	0.411	- 5.39	- 5.596
0.013 03	1		2.370	- 0.13	0.066
0.012 32	1		2.370	- 0.48	- 0.186	- 4.79	- 5.028
0.011 72	0.7		2.364	0.64	0.723	- 4.53	- 4.818
0.010 21	0.7		2.364	- 0.15	0.129	- 3.88	- 4.166
0.008 696	0.7		2.364	- 0.42	- 0.102	- 3.21	- 3.599
0.008 914	0.4229		2.358	- 0.12	0.124	- 3.60	- 3.898
0.008 478	0.1656		2.352	- 0.13	0.127	- 3.88	- 4.090
0.009 014	0		2.349	0.27	0.445	- 4.63	- 4.800
0.008 313	0		2.349	- 0.20	0.058
0.007 812	0		2.349	- 0.40	- 0.072	- 3.93	- 4.166
0.007 608	0		2.349	- 0.46	- 0.120	- 3.81	- 4.059

TABLE IV. Comparison between MD results of Ref. 5 with the one-fluid molecular plus "medianization" procedure explained in the text. The LJ parameters are those for N₂ (Ref. 4), $\sigma = 3.31$ Å, $\epsilon/k = 37.3$ K for all molecules. The density for all cases is $\rho = 0.01779$ Å⁻³. As explained in the text, the l/σ 's for N-N, N-N, and N-N are 0.1646, 0.3292, and 0.6584, respectively.

Temperature T (K)	System	\bar{l}/σ	Compressibility factor PV/NkT		Excess internal energy per molecule in units of kT U/NkT	
			This work	MD	This work	MD
102.6	Pure N-N	0.3292	2.28	1.91	- 5.89	- 3.67 ^a
99.1	Pure N-N	0.6584	19.47	14.59	- 3.77	- 3.79
101.0	Pure N-N	0.1646	- 1.66	- 0.92	- 6.60	- 6.22
108.2	Equimolar N-N/N-N	0.4150	5.40	4.45	- 5.13	- 5.03
110.9	Equimolar N-N/N-N	0.4938	9.05	6.89	- 4.50	- 4.38

^aWe believe this result to be in error.

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APPENDIX: MIXING RULES FOR HOMONUCLEAR CONFORMAL DIATOMICS

For one-component homonuclear diatomics, the energy, compressibility, and virial equations are, respectively,

$$U^{ex}/N = 2\rho \int dr g^{000}(r)\psi(r), \quad (\text{A1})$$

$$kT(\partial\rho/\partial p)_T = 1 + \rho \int dr [g^{000}(r) - 1], \quad (\text{A2})$$

$$p = \rho kT - \frac{2}{3}\rho \int dr [rg^{000}(r) - (l/\sqrt{3})g^{100}(r)] d\psi/dr \quad (\text{A3})$$

with the following analogous results for mixtures:

$$U^{ex}/N = 2\rho \sum x_i x_j \int dr g_{ij}^{000}(r)\psi_{ij}(r), \quad (\text{A4})$$

$$kT(\partial\rho/\partial p)_T = 1 + \rho \sum x_i x_j \int dr [g_{ij}^{000}(r) - 1], \quad (\text{A5})$$

$$p = \rho kT - \frac{2}{3}\rho \sum x_i x_j \int dr \times [rg_{ij}^{000}(r) - (l_{ij}/\sqrt{3})g_{ij}^{100}(r)] d\psi_{ij}/dr. \quad (\text{A6})$$

Here ρ is the total number density, x_i the fractional concentrations, $\psi_{ij}(r)$ the site-site potential energies, $g_{ij}^{000}(r)$ the site-site radial distribution functions with g_{ij}^{100} the corresponding 100 spherical harmonics, and

$$l_{ij} = \frac{1}{2}(l_i + l_j) \quad (\text{A7})$$

where l_i are the bond lengths.

We now restrict attention to site-site potential energies having the simple scaling property

$$\psi_{ij}(r) = \epsilon_{ij} \Psi(r/\sigma_{ij}). \quad (\text{A8})$$

Clearly it is possible to obtain a simple one-fluid model (analogous to the van der Waals one fluid or atomic liquids) if we assume that the g_{ij} satisfy the simple scalings

$$g_{ij}^{000}(r) = G^{000}(r/\sigma_{ij}), \quad (\text{A9})$$

$$g_{ij}^{100}(r) = G^{100}(r/\sigma_{ij}). \quad (\text{A10})$$

Both of these may be included in the single statement

$$g_{ij}(r, \Omega_1, \Omega_2) = G(r/\sigma_{ij}, \Omega_1, \Omega_2) \quad (\text{A11})$$

for the full angle-dependent site-centered correlation function. We assume the same types of scaling for the equivalent one-component homonuclear diatomic fluid, i.e.,

$$g(r, \Omega_1, \Omega_2) = G(r/\bar{\sigma}, \Omega_1, \Omega_2), \quad (\text{A12})$$

$$\psi(r) = \bar{\epsilon} \Psi(r/\bar{\sigma}). \quad (\text{A13})$$

Inserting Eqs. (A12) and (A13) in Eqs. (A1)–(A3) and (A8) and (A11) in Eqs. (A4)–(A6) followed by equating Eq. (A1) with Eq. (A4), Eq. (A2) with Eq. (A5), and Eq. (A3) with Eq. (A6) yields the following mixing rules:

$$\bar{\epsilon}\bar{\sigma}^3 = \sum x_i x_j \epsilon_{ij} \sigma_{ij}^3, \quad (\text{A14})$$

$$\bar{\sigma}^3 = \sum x_i x_j \sigma_{ij}^3, \quad (\text{A15})$$

$$\bar{\epsilon}\bar{\sigma}^3\bar{\lambda} = \sum x_i x_j \epsilon_{ij} \sigma_{ij}^3 \lambda_{ij}, \quad (\text{A16})$$

where

$$\lambda_{ij} = l_{ij}/\sigma_{ij} = (l_i + l_j)/2\sigma_{ij}. \quad (\text{A17})$$

Equations (A14) and (A15) are identical to the atomic vdW one-fluid rules and, interestingly, Eq. (A16) is just Ree's rule (5) for exponential-six monatomics with α replaced by λ .

We remark that, in the context of atomic fluids, Eq. (A14) has usually been justified by using the energy equation, or alternatively the virial equation, in a manner analogous to that described above. On the other hand, the argument leading from the compressibility equation to Eq. (A15) does not seem to have been given previously for atomic fluids. Although one cannot of course "derive" approximate mixing rules, we feel that our use of the compressibility equation is somewhat more satisfying than previous approaches. Once we decide to seek an equivalent pure fluid and make the scaling assumption for the correlation functions then requiring thermodynamic consistency leads naturally to Eqs. (A14) and (A15) [and, in the diatomic case, Eq. (A16)].

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