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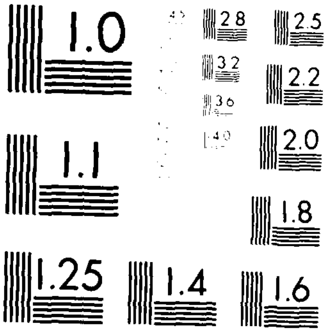

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EQUATION OF STATE AND TWO-BODY CORRELATIONS FOR FLUIDS OF NON-SPHERICAL MOLECULES

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This report is concerned with the progress made in obtaining the equation of state for fluid mixtures of non-spherical molecules beyond which was already in the previous annual report, SSS-R-84-6456, December 1983. Mixing rules and the medianization procedure were used for a CO_2-C_2H_6 and other mixtures and found to give a very concise simple theory which is in good agreement with molecular dynamics. New mixing rules for spherical non-conformal potentials were obtained in the case of the exp-6.

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A-1

1. INTRODUCTION

We report here on the progress made in our work on the thermal properties of fluids whose molecules interact via two-body non-spherical potentials.

To avoid unnecessary repetition we refer the reader to our 1983 annual report[1] and concentrate here on the new developments that took place this current year.

During the present period we directed our efforts to extending the sphericalization procedure of the median potential[2] to calculate the thermodynamics of fluid mixtures of rigid diatomic molecules.

Our approach in considering this type of fluid mixtures was to obtain an equivalent single component spherical potential. In order to do that we explored and generalized the van der Waals one fluid (vdW1f) mixing rules,[3] originally introduced to treat atomic mixtures interacting via conformal potentials. We describe this subject in Section 2. The mixing rules were used in conjunction with the modification of the median procedure that MacGowan developed for Lennard-Jones (LJ) homonuclear diatomic fluids,[4] which he calls MED (12,6).[5] In Section 3 we give an account of this "mixing rules plus medianization" procedure as applied to mixtures of diatomic homonuclear LJ molecules, for which computer simulations were available for comparison. In Section 4 we offer our conclusions.

2. VAN DER WAALS ONE-FLUID MIXING RULES AND GENERALIZATIONS

The vdW1f model is a procedure that uses a simplified potential to represent the mixture interatomic potentials. It was derived to be applied to the case of conformal interatomic potentials, i.e.,

$$\phi_{ij} = \varepsilon_{ij} \ \Phi(r/b_{ij}) \tag{1}$$

where Φ is a universal function (for example $4[\xi^{-12} - \xi^{-6}]$ for LJ atoms) and ε_{ij} and b_{ij} define the well depth and the separation at the minimum of Φ_{ij} respectively for the interaction between species i and j.

The prescription of the vdW1f approximation consists of defining an equivalent single component fluid of potential

$$\phi_x(r) = \varepsilon_x \ \Phi(r/b_x) \tag{2}$$

where the x explicitly indicates the dependence on mixture composition, and ε_x and b_x are given by

$$b_x^3 = \sum x_i \ x_j \ b_{ij}^3 \tag{3}$$

$$\varepsilon_x b_x^3 = \sum x_i \ x_j \ \varepsilon_{ij} \ b_{ij}^3 \tag{4}$$

where x_i are the fractional concentration of the components. This equivalent potential is then used to calculate the thermodynamic of the mixture. The results one obtains are very good if the spread of values of the ε_{ij}'s and b_{ij}'s is not too large. Indeed the vdW1f theory does much better than much more elaborate techniques.[6]

In the case of molecular mixtures of non-spherical rigid molecules our goal is to jointly utilize mixing rules of the sort of the vdW1f theory and the sphericalization procedure given by the median and its extension. The objective is then to obtain a single spherical "medianized" concentration dependent potential representing, for the purpose of calculating the thermodynamics, the mixture. This has certainly been our motivation in considering the mixing rules that are the object of this description.

For the particular case of binary mixtures of diatomic homonuclear LJ molecules described in Reference 1, one needs eight parameters to describe the 1-1, 1-2 and 2-2 interactions; they are $\epsilon_{ij} = \epsilon_{ji}$, $b_{ij} = b_{ji}$, and l_i, $i = 1,2$, which define entirely the LJ site-site (atom-atom) potentials of the two species.

One has at least two ways to proceed, either: (i) "to medianize" the 1-1, 1-2 and 2-2 potentials using the MED (12,6) and then to construct mixing rules for the three resulting sphericalized potentials; or (ii) to define mixing rules to obtain ϵ_x, b_x and l_x which define a single component diatomic homonuclear LJ molecular fluid and the "medianize" it using MED (12,6).

Clearly, the results one would obtain by using (i) or (ii) will not be the same. The advantage of procedure (i) is that, at least in principle, one could extend this type of reasoning to treat mixtures of molecules other than homonuclear diatomics. That one can do provided one has a well defined medianization technique for such potentials. One should bear in mind that this is not an obvious task when the molecules do not possess a center of symmetry, and it has only been done for diatomic non-homonuclear hard dumbells.[7]

Even in the simple case of homonuclear diatomics LJ mixture we are describing, in which the site-site potentials are conformal, the resulting medianized ones are not of the same shape. Therefore, one must deal in general with non-conformal spherical potentials, i.e.,

$$\phi_{ij} = \epsilon_{ij} \ \Phi(r/b_{ij}, \underline{\alpha_{ij}}) \tag{5}$$

where ϵ_{ij} and b_{ij} have the same meaning as before as $\underline{\alpha_{ij}}$ is a set of parameters introduced to characterize the difference in shapes of the ϕ_{ij}'s.

An important realization of Eq. (5) is the exponential -6 (exp-6) potential where there is only a single parameter α_{ij} for each ϕ_{ij} and

$$\Phi(\xi,\alpha) = 6 \exp[\alpha(1-\xi) - \alpha\xi^{-6}]/(\alpha-6).$$

Ree[8] has recently found that for mixtures of exp-6 atoms - he modeled an H_e-H_2 mixture at high temperatures and densities -, the mixing rules of Eqs. (3) and (4) and the following extra mixing rule for α_x is very successful:

$$\alpha_x \varepsilon_x b_x^3 = \sum x_i \; x_j \; \alpha_{ij} \; \varepsilon_{ij} \; b_{ij}^3 \tag{6}$$

With MacGowan and Lebowitz we researched the possibility of making the formulation of mixing rules more systematic. We found that for the case of conformal atomic LJ potentials we were able to clarify how the rules of Eqs. (3) and (4) come about by use of approximate scaling arguments on the radial distribution functions g_{ij} in the compressibility, energy and virial equations. For the case of exp-6 potentials by expanding to second order the potential around its minimum in a Taylor series and employing again approximate scaling arguments on the g_{ij}'s, we show how one can generate various alternative mixing rules for ε_x b_x and α_x. One such set produces thermodynamic results of accuracy equivalent to that of Ree's work. The details of this work are contained in Appendix A, which is a preprint of an article submitted and accepted for publication in Chemical Physics Letters.

This is the present status on this approach. Up to now to have not applied this procedure (i) to molecular mixtures. Before leaving this section we remark that our work on mixing rules for non-conformal spherical potentials is a contribution in its own right for such fluid mixtures (as in the case of the exp-6), and not just an intermediate step in "procedure (i)" for molecular mixtures. We explain procedure (ii) next.

3. A ONE MOLECULAR FLUID APPROXIMATION FOR DIATOMIC FLUID MIXTURES

We considered a CO_2-C_2H_6 mixture, treated as rigid homonuclear diatomic LJ molecules, for which computer simulations were available.[9] Because it happens in this case that the bond lengths are very similar, $l_1 \approx l_2 \approx 2.36$ Å, it occurred to us to apply procedure (ii) as defined in Section 2. That is: We first find ϵ_x, b_x abd l_x which define a single component equivalent homonuclear diatomic LJ fluid and then apply to it MED (12,6). For ϵ_x and b_x we used the mixing rules of Eqs. (3) and (4). For l_x any reasonable rule would give essentially identical results, we chose

$$l_x = \sum x_i \, l_i \qquad (7)$$

The MED (12,6) $\phi_x(r)$ potential was utilized then in Ross's variational procedure[10] for obtaining the free energy and from it the pressure and internal energies of the mixture. The results compare favorably with those of the computer simulations, which is remarkable considering the calculational simplicity of our formulation. (It takes 1 second of CPU time of a DEC20 computer per thermodynamic ρ,T point.)

We also applied this technique to equimolar binary mixtures of rigid homonuclear diatomic mixtures, of molecules denoted as N.N, N-N and N--N by the researchers that did molecular dynamics calculations employing them.[11] They all have $\epsilon_{ij} = \epsilon_{N_2}$, $b_{ij} = b_{N_2}$, i,j = 1,2, where ϵ_{N_2} and b_{N_2} are the parameters used to represent N_2. In this nomenclature N-N is identical to N_2 and has an elongation l/σ of 0.3292 while N.N and N--N have half and twice that elongation, respectively. Here σ is the point at which the LJ potential crosses the axis and is related to b by $b = 2^{1/6}\,\sigma$. The mixing rules for ϵ_x and b_x obviously give ϵ_{N_2} and b_{N_2} while for this equimolar mixtures Eq. (6) gives the arithmetic mean of l_1 and l_2. The sparcity, and some errors we believe to exist in the reported data by the authors of Reference 11, do not permit us to draw definite conclusions in this case.

We also developed an alternative mixing rule to that of Eq. (6) using the systematic approach described in Appendix A for atomic systems, and in Appendix B for the system under consideration. By employing arguments of approximate scaling for the g_{ij}'s in the virial equation for these diatomic mixtures we obtained

$$\varepsilon_x b_x^3 \lambda_x = \sum x_i \; x_j \; \varepsilon_{ij} \; b_{ij}^3 \; \lambda_{ij} \tag{8}$$

where $\lambda_{ij} \equiv (l_i + l_j)/2b_{ij}$.

In the cases reported in this section the values of l_x obtained with Eq. (8) are either identical or almost identical to that of Eq. (6). To text the mixing rule of Eq. (8) one needs to compare its results with computer simulations with $l_1 \neq l_2$ and $x_1 \neq x_2$ which are not presently available.

We include in Appendix B a detailed account of the work described in this section, which is a preprint of a paper with Lebowitz and MacGowan scheduled for publication in the December 15, 1984 issue of Journal of Chemical Physics.

4. CONCLUSIONS

Very significant progress has been made in extending the idea of the median potential to obtain the fluid thermodynamic property mixtures of rigid diatomic homonculear molecules. Also we have made a contribution in clarifying and generalizing mixing rules for atomic and molecular mixtures.

We expect to be able to continue to make significant advances in treating mixtures of diatomic and monoatomic species as well as mixtures containing other simply shaped rigid symmetrical molecules, such as those of tetrahedral structure.

5. REFERENCES

1. Waisman, E. M., "Equation of State and Two-Body Correlations for Fluids of Non-Spherical Molecules," S-CUBED Annual Report, SSS-R-84-6456, December 1983.

2. Lebowitz, J. L. and J. K. Percus, J. Chem. Phys. 79, 443 (1983); M. S. Shaw, J. D. Johnson and B. L. Holian, Phys. Rev. Lett. 50, 1141 (1983).

3. MacGowan, D., J. Chem. Phys. (to be published).

4. MacGowan, D., J. Chem. Phys. 81, 3224 (1984).

5. Notice there is a slight change of nomenclature with respect to our 1984 proposal, SSS-P-84-8520212, "Equation of State and Two-Body Correlations for Fluids of Non-spherical Molecules," where we called the procedure MED (6,12).

6. Henderson, D., Annu. Rev. Phys. Chem. 25, 461 (1974).

7. Williams, G. O., J. L. Lebowitz and J. K. Percus, J. Phys. Chem. (to be published).

8. Ree, F. H., J. Chem. Phys. 78, 409 (1983).

9. Fincham, D., N. Quirke and D. J. Tildesley (to be published).

10. Ross, M., J. Chem. Phys. 71, 1567 (1979).

11. Nakanishi, K. and H. Tanaka, Fluid Phase Equilibria 13, 371 (1983).

APPENDIX A

VAN DER WALLS ONE-FLUID THEORY: JUSTIFICATION AND GENERALIZATION

A ONE MOLECULAR FLUID APPROXIMATION FOR DIATOMIC FLUID MIXTURES

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Abstract

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.

1. 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 [illegible], no means a priori obvious the results on spherical single component fluids and "some" mixtures [1] strongly suggest the possibility. This motivates

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APPENDIX B

A ONE MOLECULAR FLUID APPROXIMATION FOR DIATOMIC FLUID MIXTURES

Table

			Mixture	Equivalent pure fluids			
T (K)	V (cm^3/mol)	x_1		Ree	I	II	III
50	20.0	0.50	0.047	0.048	0.048	0.049	0.055
			-0.755	-0.736	-0.737	-0.725	-0.669
100	14.0	0.50	0.338	0.337	0.336	0.339	0.365
			-0.354	-0.334	-0.336	-0.318	-0.202
300	10.0	0.50	1.856	1.858	1.850	1.872	2.001
			2.79	2.91	2.90	2.94	3.28
		0.75	2.309	2.315	2.307	2.327	2.472
			3.49	3.65	3.64	3.68	4.07
		0.25	1.424	1.417	1.413	1.425	1.484
			2.08	2.11	2.10	2.12	2.27
1000	9.0	0.50	4.510	4.416	4.397	4.452	4.734
			8.86	8.85	8.82	8.91	9.52
		0.75	5.255	5.172	5.155	5.202	5.504
			10.88	10.86	10.83	10.91	11.60
		0.25	3.715	3.643	3.634	3.665	3.801
			6.79	6.70	6.69	6.73	7.01
4000	8.0	0.50	12.43	12.15	12.10	12.26	12.98
			25.12	24.82	24.74	24.96	26.31
4000	7.0	0.50	16.33	15.96	15.89	16.13	17.21
			31.4	31.1	31.0	31.3	33.2
7000	4.5	0.50	54.01	52.53	52.15	53.39	58.48
			84.7	85.3	84.8	86.1	92.5
		0.75	56.21	54.54	54.18	55.26	60.58
			97.2	98.2	97.8	98.8	105.1
		0.25	48.83	47.52	47.32	48.06	50.65
			68.0	66.6	66.4	67.1	70.4

Table Caption

Thermodynamic results for binary mixtures of exponential-six fluids representing hydrogen-helium mixtures [11]. The potential parameters are ϵ_{11}/k_B=36.4K, b_{11}=3.43Å, α_{11}=11.1, ϵ_{12}/k_B=15.5K, b_{12}=3.37Å, α_{12}=12.7, ϵ_{22}/k_B=10.57K, b_{22}=2.97Å, α_{22}=13.6, where the subscript 1 denotes hydrogen. In each row the upper results are pressures(GPa) and the lower results are excess internal energies(kJ/mol). Results in the columns headed Mixture and Ree are from 256-particle Monte-Carlo simulations [11]. Results in the columns headed I, II and III were obtained by using Ross' procedure [12] in the perturbative manner described in the text.

References

[1] For a recent review see K. E. Gubbins, K. S. Shing and W. B. Streett, J. Phys. Chem. 87 (1983) 4573.

[2] T. W. Leland, P. S. Chappelear and B. W. Gamson, Amer. Inst. Chem. Eng. J. 8 (1962) 482.

[3] D. Henderson and P. J. Leonard, Proc. Nat. Acad. Sci. U.S.A. 68 (1971) 632.

[4] T. W. Leland, J. S. Rowlinson and G. A. Sather, Trans. Farad. Soc. 64 (1968) 1447.

[5] W. R. Smith, Can. J. Chem. Eng. 50 (1972) 271.

[6] D. Henderson and P. J. Leonard, Proc. Nat. Acad. Sci. U.S.A. 67 (1970) 1818.

[7] D. J. Evans and H. J. M. Hanley, Phys. Rev. A 20 (1979) 1648.

[8] E. M. Waisman, J. L. Lebowitz and D. MacGowan, J. Chem. Phys. submitted.

[9] G. C. Maitland, M. Rigby, E. B. Smith and W. A. Wakeham, *Intermolecular Forces* (Clarendon, Oxford, 1981); especially Chapter 9 and Appendix 1.

[10] D. MacGowan, J. Chem. Phys. in press.

[11] F. H. Ree, J. Chem. Phys. 78 (1983) 409.

[12] M. Ross, J. Chem. Phys. 71 (1979) 1567.

states simulated by Ree but inferior to both I and Ree's empirical rules at low temperatures. We do not, however, regard the small changes in accuracy between Ree, I and II as very significant. More important is our hope that our approach to the mixing rules will prove useful for application in the manner indicated above to non-conformal potentials other than exponential-six.

Acknowledgements

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$$g_x(r) = \tilde{G}(\alpha_x r/b_x) \qquad (12)$$

Substituting these relations in the compressibility and energy (or virial) equations yields the MRs

III $\langle b^3\alpha^{-3}\rangle$, $\langle \epsilon b^3\alpha^{-3}e^{-\alpha}/(\alpha-6)\rangle$, $\langle \epsilon b^3\alpha^4/(\alpha-6)\rangle$

without any need to consider only the part of the potential near its minimum. Unfortunately, (11) and (12) have the opposite effect to what is expected physically at high pressures: they indicate a principal peak in g(r) at larger r for softer potentials (i.e. lower α).

Ideally one would like to test the MRs proposed above by simulations, as Ree did, but another reliable method for the EPFs is Ross' semi-empirical variational procedure [12], which we have used to obtain the tabulated results. Although Ross' procedure is accurate to only 1-2% in absolute terms (and seems to deteriorate further at very high pressures), we believe that it can accurately distinguish much smaller *differences* between thermodynamic properties of similar potentials at the same temperature and density. Thus the tabulated results are based on the assumption that the change in exact EPF thermodynamics between Ree's MRs and I, II or III is equal to the corresponding change in the Ross thermodynamics.

On the basis of these results we conclude that III gives energies and pressures which are consistently too high, I is (not unexpectedly) best at low temperatures but deteriorates as the temperature increases, and II is on average best over the full range of important in determining the energy and virial equation integrals. We therefore use in the energy (or virial) equation the Taylor expansion of $\phi_{ij}(r)$ about b_{ij} and demand only that EPF and mixture results obtained by integrating the first two non-vanishing terms of the expansion should be identical. Apart from the excluded volume MR $<b^3>$, which is still obtained exactly as before from consideration of the compressibility equations, this procedure leads to the MRs

$$\mathrm{I} \qquad <\epsilon b^3> \;,\; <\epsilon b^3\alpha(\alpha-7)/(\alpha-6)>$$

if the energy equation is used or

$$\mathrm{II} \qquad <\epsilon b^3\alpha(\alpha-7)/(\alpha-6)> \;,\; <\epsilon b^3\alpha(\alpha^2-56)/(\alpha-6)>$$

when the virial equation is used.

Rules I give the same ϵ_x and b_x as the vdW1 rules and, since the α_{ij} are all in the range 11-14, an α_x very close to but slightly lower than the value obtained by Ree. The functions of α appearing in the MRs are just $|\Phi^{(k)}(\xi=1,\alpha)|$, k=0,2,3, where $^{(k)}$ denotes the kth derivative with respect to ξ. A straightforward generalisation when there is more than one shape parameter would be to obtain the extra MRs necessary in an analogous way from higher derivatives.

For exponential-six potentials it might seem attractive, from a purely mathematical viewpoint, to assume instead of (5) and (6) the scalings

$$g_{ij}(r) = \bar{G}(\alpha_{ij}r/b_{ij}) \qquad (11)$$

and

3. Generalisation

One generalisation of vdW1 theory to mixtures of conformal diatomic molecules has recently been proposed [8] but we shall be concerned here only with non-conformal spherical molecules. There are at least two reasons why one may wish to study such mixtures. First, real fluids are not satisfactorily represented by conformal potentials [9] and, second, the effective spherical potentials which can be used to accurately reproduce thermodynamics of some non-spherical molecules are not in general conformal even when the original molecular potentials are [10].

We continue to scale the interactions according to their minima, as in the conformal case, but now allow for differences between the shapes of the ϕ_{ij} through the introduction of a set of parameters $\underline{\alpha}_{ij}$:

$$\phi_{ij}(r) = \epsilon_{ij}\,\Phi(r/b_{ij}\,,\,\underline{\alpha}_{ij}) \qquad (10)$$

The simplest and, for present purposes, the most relevant realisation of (9) is the exponential-six potential where there is only a single parameter α_{ij} for each ϕ_{ij} and $\Phi(\xi,\alpha)=\{6\exp[\alpha(1-\xi)]-\alpha\xi^{-6}\}/(\alpha-6)$. Ree [11] has recently found quite empirically that for exponential-six mixtures the MRs $\langle b^3\rangle$, $\langle \epsilon b^3\rangle$ and $\langle \epsilon b^3\alpha\rangle$ lead to results as good as those of vdW1 theory for Lennard-Jones mixtures.

We wish to retain the assumptions (5) and (6), which are physically reasonable at low pressures, but observe that with these assumptions and an exponential-six pair potential no simple scaling of the energy and virial integrals occurs. At low temperatures near to the triple point, however, we expect the region around the minimum of the potential (coinciding with the main peak of the radial distribution function) to be most

Here an ambiguity occurs: if A_{ij} is considered as an energy, vdW1 yields the MR <A> but it can equally well be considered as (potential range)$^{\nu}$ leading to the MR $<A^{3/\nu}>$. The latter rule was used by Evans and Hanley [7] for $\nu=12$ and gave good agreement with simulations. It was also used in [4] where the VdW1 results for inverse power potentials were shown to be quite close to those obtained from a first order expansion in $1/\nu$ about the Percus-Yevick equation of state for binary hard sphere mixtures.

term to g(r) from Eqs. (5) and (6) which is the first order of a formally exact series in powers of $\beta\epsilon$:

$$g(r) = G(r/b) \{ 1 + \beta\epsilon H(r/b) + \cdots \} \tag{7}$$

where H is assumed to be 'universal' in the same sense as G. Using (7), Leland *et al.* [2] claim to obtain both of Eqs. (3) and (4) from consideration of the energy (or virial) equation but in fact it seems clear that one obtains Eq. (4) together with the MR $<\epsilon^2 b^3>$.

We believe that a more satisfactory way of obtaining (3) is by an appeal to thermodynamic consistency. If we substitute (5) and (6) in the compressibility equation

$$\beta^{-1}(\partial\rho/\partial p)_\beta = 1 + \rho \sum x_i x_j \int d\underline{r} \{ g_{ij}(r) - 1 \} \tag{8}$$

for both the mixture and the EPF and demand that both give the same result, we obtain Eq. (3). [We remark, incidentally, that substituting (7) in the *compressibility* equations really does yield both (3) and (4)]. Thus we see that once we have decided to represent a conformal mixture by a conformal EPF and made the assumptions (5) and (6), we are naturally driven to choose the vdW1 MRs for reasons of thermodynamic consistency.

For pair potentials determined by a single parameter only one MR is needed. In such cases the excluded volume MR (3) seems to be more important than the energy MR (4). This is very natural for hard sphere mixtures where the potential has no energy scale and the $<d^3>$ MR, which for hard spheres could arise from consideration of either the virial or compressibility equations, is successful [6]. Less obviously, it also seems to be true for inverse power law potentials

$$\phi_{ij}(r) = A_{ij}/r^\nu = \epsilon_{ij}(\sigma_0/r)^\nu = \epsilon_0(\sigma_{ij}/r)^\nu \ , \ \nu>3 \tag{9}$$

2. Justification

Clearly one cannot expect to 'derive' VdW1 theory but there have been various attempts to understand its success. Leland et al. [4] note that it arises naturally from the vdW equation of state by (hence the name VdW1) but emphasize that its applicability is not confined to fluids satisfying the VdW equation of state. Smith [5] has given a general perturbation theory based on the reference EPF obtained with $\langle \varepsilon^m b^n \rangle$ and $\langle \varepsilon^p b^q \rangle$ MRs, which allows systematic corrections, but this gives no insight into why the choice $(m,n,p,q)=(0,3,1,3)$ should be especially accurate.

Other explanations have been based upon the *assumption* that the suitably scaled radial distribution functions of both the mixture and the EPF have the same form, i.e.

$$g_{ij}(r) = G(r/b_{ij}) \tag{5}$$

and

$$g_x(r) = G(r/b_x), \tag{6}$$

where the function G can depend on the temperature $T=(k_B\beta)^{-1}$ and the total number density ρ although these arguments are not shown explicitly. If relations (1), (2), (5) and (6) are substituted in the energy (or virial) equations for both the mixture and EPF, then the requirement that both expressions be equal leads to Eq. (4) [2,3]. This seems to be as satisfactory a justification of Eq. (4) as one can hope to get, but the arguments used by these authors for Eq. (3) seem flawed by comparison.

Henderson and co-workers [3] merely take over Eq. (3) from the similar $\langle d^3 \rangle$ MR (d represents sphere diameter) arising from consideration of the virial equation for hard sphere mixtures [6]. Leland *et al.* [2], on the other hand, in effect use a correction

1. Introduction

Fluid mixtures are of great practical importance but theoretical calculations for them are generally much harder than for single species [1]. An exception is mixtures of conformal spherical molecules not too different in size having pair interactions of the form

$$\phi_{ij}(r) = \epsilon_{ij}\,\Phi(r/b_{ij}) \tag{1}$$

where Φ is a universal function and ϵ_{ij} and b_{ij} define the well depth and the separation at its minimum respectively for the interaction between species i and j. For such mixtures, the van der Waals one-fluid (vdW1) theory [2] is believed to be much better for predicting thermodynamics than many more complicated approximations although this has admittedly only been tested for Lennard-Jones mixtures with $\Phi(\xi)=\xi^{-12}-2\xi^{-6}$ [3]. In vdW1 theory, the mixture is replaced by an equivalent pure fluid (EPF) with pair interaction

$$\phi_x(r) = \epsilon_x\,\Phi(r/b_x). \tag{2}$$

Here the EPF parameters are defined by

$$b_x^{\,3} = \sum x_i x_j b_{ij}^{\,3} \tag{3}$$

and

$$\epsilon_x b_x^{\,3} = \sum x_i x_j \epsilon_{ij} b_{ij}^{\,3} \tag{4}$$

where x_i are the fractional concentrations of the components. We shall have occasion to refer to many different mixing rules (MRs) of this general form and so for brevity we refer to (3) and (4) in an obvious notation as the MRs $<b^3>$ and $<\epsilon b^3>$.

VAN DER WAALS ONE-FLUID THEORY: JUSTIFICATION AND GENERALISATION

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Abstract

We describe an approach to van der Waals one-fluid theory based on thermodynamic consistency and propose a method for generalising it to non-conformal fluids.

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the search for similar procedures for non-spherical 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 non-polar one component diatomics [2]. It is the purpose of this note to investigate a simple scheme for mixtures of such molecules.

2. Formulation of the Problem

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

$$v_{ij}(R,\underset{\sim}{\Omega}_1,\underset{\sim}{\Omega}_2) = \sum_{\pm} \psi_{ij}(|\underset{\sim}{R} \pm 1/2\, \ell_i \underset{\sim}{\Omega}_1 \pm 1/2\, \ell_j \underset{\sim}{\Omega}_2|) \, , \qquad (1)$$

where $\underset{\sim}{R}$ is the vector between the centers of molecule 1 of species i and molecule 2 of species j, and $\underset{\sim}{\Omega}_k$, k=1,2, is a unit vector along the axis of molecule k. ℓ_i and ℓ_j are the bondlengths 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

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

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 a 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, [illegible] for

N_2 denoted in [5] by N-N is 0.3292 while ℓ/σ = 0.1646 and ℓ/σ = 0.6584 respectively for the molecules denoted in [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 L-J molecules where MacGowan [7] found that the best modified median is obtained by splitting the potential in (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 [10] for "hard" mixtures of dumbells, 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 1-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 $\bar{\epsilon}\Phi(r/\bar{\sigma})$,

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

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

is at least as accurate as much more elaborate procedures. This mixing rule has been extended recently by Ree [11] to mixtures of particles interacting via exponential-six potentials 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 (3) and (4) the rule

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

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 $v_{ij}(R,\underset{\sim}{\Omega}_1,\underset{\sim}{\Omega}_2)$ are not generally given by a simple formula for which (3) and (4) can be used directly. This is true even for the case in Eq. (1)-(2). It therefore occurred to us that since the site-site potentials in (2) are of simple form it is worth trying a molecular 1-fluid theory in which $\bar{\sigma}$ and $\bar{\epsilon}$ would still be given by (3) and (4), and $\bar{\chi}$ would be given by a suitable mixing rule. In the present work we exclusively use the simple rule

$$\bar{\ell} = \sum x_i \ell_i \tag{6}$$

for the equivalent bondlength.

A plausibility argument is given in the Appendix for a more complicated rule (A.16) for $\bar{\ell}$, similar to (5), but for all mixtures where simulations are available the $\bar{\ell}$'s obtained from (6) and (A.16) are almost identical (in many cases exactly so). For the computer simulations of the CO_2 - C_2H_6 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 $\bar{\ell}$. For the mixtures of [5], on the other hand, one is just testing the mixing rule (6) for $\bar{\ell}$. Unfortunately the number of available results is not sufficient to permit, at this time, testing of different possibilities for $\bar{\ell}$ and indeed there appears to be at least one misprint among the published data in [5]. Additional computer simulations systematically varying the parameters ε_{ij}, σ_{ij}, ℓ_i and x_i would be most useful.

3. Results

With the $\bar{\varepsilon}$, $\bar{\sigma}$ and $\bar{\ell}$ given by Eqs. (3), (4), and (6), we sphericalize using MacGowan's procedure [7] for diatomic Lennard-Jones potentials and use the resulting spherical potential in Ross' semi-empirical variational procedure [12] 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 one second of CPU time on a DEC 20 computer per thermodynamic point.

We compare the available results of molecular dynamics simulations of CO_2-C_2H_6[3] with our calculations in Tables I, II and III. Since the molecular dynamics calculations for CO_2-C_2H_6 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 through III corresponding to different values of those parameters, at a few different thermodynamic points.

Our results for the CO_2-C_2H_6 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 CO_2 and C_2H_6 fluids. Also the tendencies for our calculated values are the same as for the simulations.

We show in Table IV the comparison between this 1-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 [5] by N--N, N-N and N.N and all have the same ϵ and σ as N_2. The few results available do not allow us to draw any firm conclusion. We believe that the excess internal energy reported in [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-1-fluid approximation now in use for mixtures of spherical molecules to mixtures of non-spherical molecules.

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Table I

Number Density $\rho[\mathring{A}^{-3}]$	Concentration of CO_2 x_1	$\bar{\ell}(\mathring{A})$	$\sigma_{22}(\mathring{A})$	$\sigma_{12}(\mathring{A})$	$\epsilon_{12}/k(°K)$	Compressibility Factor PV/NkT 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

Comparison between the molecular dynamics (MD) calculations [3] and the "medianized" 1-f molecular approximation explained in the text for a mixture of CO_2 (subindex 1) - C_2H_6 treated as rigid Lennard-Jones diatomics with $\ell_1 = 2.370$ Å and $\ell_2 = 2.349$ Å. The compressibility factors are near zero so that small absolute differences are large in relative terms. The temperature was $T = 241$ °K, $\sigma_{11} = 2.989$ Å, $\epsilon_{11}/k = 163.6$ °K, $\epsilon_{22}/k = 137.5$ °K.

*These three values are ℓ_1, $(\ell_1+\ell_2)/2$ and ℓ_2 respectively. They are included to see how our results in a particular case are altered by varying $\bar{\ell}$ from ℓ_1 to ℓ_2.

Table II

Number Density $\rho[\mathring{A}^{-3}]$	Concentration of CO_2 x_1	$\bar{l}(\mathring{A})$	ϵ_{12}/k °K	Compressibility Factor PV/NkT		Excess Internal Energy per Molecule in Units of kT U/NkT	
				This Work	MD	This Work	MD
0.00833	0.00	2.349	149.85	0.02	0.059	-4.55	-4.421
0.01302	1.00	2.370	149.85	-0.13	0.066	-5.11	-5.324
0.01023	0.70	2.364	149.85	-0.54	-0.226	-4.41	-4.573
0.01023	0.70	2.364	120.0	-0.08	0.099	-3.98	-4.149

Same as Table I. $T = 269.3$ °K, $\sigma_{11} = 3.035\ \mathring{A}$, $\sigma_{22} = 3.592\ \mathring{A}$, $\sigma_{12} = 3.3135\ \mathring{A}$, $\epsilon_{11}/k = 163.3$ °K, $\epsilon_{22}/k = 137.5$ °K.

Table III

Number Density $\rho[\text{Å}^{-3}]$	Concentration of CO_2 x_1	$\bar{\ell}$(Å)	Compressibility Factor PV/NkT		Excess Internal Energy per Molecule in Units of kT U/NkT	
			This Work	MD	This Work	MD
0.01369	1	2.370	0.33	0.411	-5.39	-5.596
0.01303	1	2.370	-0.13	0.066	-	-
0.01232	1	2.370	-0.48	-0.186	-4.79	-5.028
0.01172	0.7	2.364	0.64	0.723	-4.53	-4.818
0.01021	0.7	2.364	-0.15	0.129	-3.88	-4.166
0.008696	0.7	2.364	-0.42	-0.102	-3.21	-3.599
0.008914	0.4229	2.358	-0.12	0.124	-3.60	-3.898
0.008478	0.1656	2.352	-0.13	0.127	-3.88	-4.090
0.009014	0	2.349	0.27	0.445	-4.63	-4.800
0.008313	0	2.349	-0.20	0.058	-	-
0.007812	0	2.349	-0.40	-0.072	-3.93	-4.166
0.007608	0	2.349	-0.46	-0.120	-3.81	-4.059

Same as Table I. T = 269.25 °K. The Lennard-Jones parameters are σ_{11} = 3.035 Å, σ_{22} = 3.520 Å, σ_{12} = 3.2775 Å, and ϵ_{11}/k = 163.29 °K, ϵ_{22}/k = 137.49 °K, ϵ_{12}/k = 120 °K. The uncertainty in the MD compressibility factors is estimated to be ± 0.01.

Table IV

Temperature T °K	System	$\bar{\ell}/\sigma$	Compressibility Factor PV/NkT This Work	MD	Excess Internal Energy per Molecule in Units of kT U/NkT This Work	MD
102.6	pure N-N	0.3292	2.28	1.91	-5.89	-3.67 [†]
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

Comparison between MD results of [5] with the 1-f molecular plus "medianization" procedure explained in the text. The L-J parameters are those for N_2 [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 text, the ℓ/σ's for N.N, N-N and N--N are 0.1646, 0.3292 and 0.6584 respectively.

[†] We believe this result to be in error.

REFERENCES

1. D. Henderson, Annual Review of Physical Chemistry, 25, 461 (1974); T. W. Leland, P. S. Chappelear, and B. W. Gamson, AIChE J. 8, 482 (1962); T. W. Leland, J. S. Rowlinson, and G. A. Sather, Trans. Faraday Soc. 64, 1447 (1968). For a recent review on fluid mixtures see K. E. Gubbins, K. S. Shing, and W. B. Street, J. Phys. Chem. 87, 4573 (1983).
2. D. MacGowan, E. M. Waisman, J. L. Lebowitz and J. K. Percus, J. Chem. Phys. 80, 2719 (1984).
3. D. Fincham, N. Quirke and D. J. Tildesley, to appear. We thank these authors for making the results of their calculation available to us prior to publication.
4. P.S.Y. Cheung and J. G. Powles, Mol. Phys. 30, 921 (1975).
5. K. Nakanishi and H. Tanaka, Fluid Phase Equilibria 13, 371 (1983).
6. J. L. Lebowitz and J. K. Percus, J. Chem. Phys. 79, 443 (1983); M. S. Shaw, J. D. Johnson, and B. L. Holian, Phys. Rev. Lett. 50, 1141 (1983)
7. D. MacGowan, to be published in J. Chem. Phys.
8. G. O. Williams, J. L. Lebowitz and J. K. Percus, J. Chem. Phys. 81, 2070 (1984).
9. C. G. Gray and C. G. Joslin, Chem. Phys. Lett. 101, 248 (1983).
10. G. O. Williams, J. L. Lebowitz and J. K. Percus, to be published in J. Phys. Chem.
11. F. H. Ree, J. Chem. Phys. 78, 409 (1983).
12. M. Ross, J. Chem. Phys. 71, 1567 (1979).

APPENDIX

MIXING RULES FOR HOMONUCLEAR CONFORMAL DIATOMICS

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

$$U^{ex}/N = 2\rho \int d\underset{\sim}{r}\; g^{000}(r)\psi(r) \tag{A.1}$$

$$kT(\partial\rho/\partial p)_T = 1 + \rho \int d\underset{\sim}{r}\; [g^{000}(r) - 1] \tag{A.2}$$

$$p = \rho kT - \frac{2}{3}\rho \int d\underset{\sim}{r}\; [r\, g^{000}(r) - (\ell/\sqrt{3})\, g^{100}(r)]\, d\psi/dr \tag{A.3}$$

with the following analogous results for mixtures:

$$U^{ex}/N = 2\rho \sum x_i x_j \int d\underset{\sim}{r}\; g_{ij}^{000}(r)\; \psi_{ij}(r) \tag{A.4}$$

$$kT(\partial\rho/\partial p)_T = 1 + \rho \sum x_i x_j \int d\underset{\sim}{r}\; [g_{ij}^{000}(r) - 1] \tag{A.5}$$

$$p = \rho kT - \frac{2}{3}\rho \sum x_i x_j \int d\underset{\sim}{r}\; [r g_{ij}^{000}(r) - (\ell_{ij}/\sqrt{3}) g_{ij}^{100}(r)]\; d\psi_{ij}/dr \tag{A.6}$$

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

$$\ell_{ij} = \frac{1}{2}(\ell_i + \ell_j) \tag{A.7}$$

where ℓ_i are the bondlengths.

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

$$\psi_{ij}(r) = \epsilon_{ij}\, \Psi(r/\sigma_{ij}) \tag{A.8}$$

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

$$g_{ij}^{000}(r) = G^{000}(r/\sigma_{ij}) \tag{A.9}$$

$$g_{ij}^{100}(r) = G^{100}(r/\sigma_{ij}) \ . \tag{A.10}$$

Both of these may be included in the single statement

$$g_{ij}(r, \underset{\sim}{\Omega}_1, \underset{\sim}{\Omega}_2) = G(r/\sigma_{ij}, \underset{\sim}{\Omega}_1, \underset{\sim}{\Omega}_2) \tag{A.11}$$

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

$$g(r, \Omega) = G(r/\bar{\sigma}, \underset{\sim}{\Omega}_1, \underset{\sim}{\Omega}_2) \tag{A.12}$$

$$u(r) = \bar{\epsilon} \ \Psi(r/\bar{\sigma}) \tag{A.13}$$

Inserting (A.12) and (A.13) in (A.1)-(A.3) and (A.8) and (A.11) in (A.4)-(A.6) followed by equating (A.1) with (A.4), (A.2) with (A.5) and (A.3) with (A.6) yields the following mixing rules:

$$\bar{\epsilon} \ \bar{\sigma}^3 = \sum x_i x_j \ \epsilon_{ij} \sigma_{ij}^3 \tag{A.14}$$

$$\bar{\sigma}^3 = \sum x_{ij} \ \sigma_{ij}^3 \tag{A.15}$$

$$\bar{\epsilon} \ \bar{\sigma}^3 \bar{\lambda} = \sum x_i x_j \ \epsilon_{ij} \sigma_{ij}^3 \ \lambda_{ij} \tag{A.16}$$

where

$$\lambda_{ij} = \ell_{ij}/\sigma_{ij} = (\ell_i + \ell_j)/2\sigma_{ij} \tag{A.17}$$

Eqs. (A.14) and (A.15) are identical to the atomic vdW 1f rules and, interestingly, (A.16) is just Ree's rule (5) for exponential-six monatomics with α replaced by λ.

We remark that, in the context of atomic fluids, (A.14) 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 (A.15) 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. (A.14) and (A.15) [and, in the diatomic case, (A.16)].