

VAN DER WAALS ONE-FLUID THEORY: JUSTIFICATION AND GENERALISATION

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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.

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

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

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 (vdWI) 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 vdWI theory, the mixture is replaced by an equivalent pure fluid (EPF) with pair interaction

$$\phi_x(r) = \epsilon_x \Phi(r/b_x). \quad (2)$$

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Here the EPF parameters are defined by

$$b_x^3 = \sum x_i x_j b_{ij}^3 \quad (3)$$

and

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

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 $\langle b^3 \rangle$ and $\langle \epsilon b^3 \rangle$.

2. Justification

Clearly one cannot expect to "derive" vdWI 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 (hence the name vdWI) but emphasise 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 $\langle \epsilon^m b^n \rangle$ and $\langle \epsilon^p b^q \rangle$ 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.

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

and

$$g_x(r) = G(r/b_x), \quad (6)$$

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 mixture [6]. Leland et al. [2], on the other hand, in effect use a correction term to $g(r)$ from eqs. (5) and (6) which is the first order of a formally exact series in powers of $\beta\epsilon$:

$$g(r) = G(r/b) [1 + \beta\epsilon H(r/b) + \dots], \quad (7)$$

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 $\langle \epsilon^2 b^3 \rangle$.

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

$$\beta^{-1}(\partial\rho/\partial p)_\beta = 1 + \rho \sum_i x_i x_j \int dr [g_{ij}(r) - 1] \quad (8)$$

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 $\langle d^3 \rangle$ 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

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

Here an ambiguity occurs: if A_{ij} is considered as an energy, vdW1 yields the MR $\langle A \rangle$ but it can equally well be considered as $(\text{potential range})^\nu$ leading to the MR $\langle A^{3/\nu} \rangle$. The latter rule was used by Evans and Hanley [7] for $\nu = 12$ and gave good agreement with simulations. It was also used in ref. [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.

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 (see ref. [9], and especially ch. 9 and appendix I therein) and, second, the effective spherical potentials which can be used to reproduce accurately 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 α_{ij} :

$$\phi_{ij}(r) = \epsilon_{ij} \Phi(r/b_{ij}, \alpha_{ij}). \quad (10)$$

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 ex-

potential-six mixtures the MRs $\langle b^3 \rangle$, $\langle eb^3 \rangle$ and $\langle eb^3 \alpha \rangle$ 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 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 $\langle b^3 \rangle$, which is still obtained ex-

Table 1

Thermodynamic results for binary mixtures of exponential-six fluids representing hydrogen-helium mixtures [11]. The potential parameters are $\epsilon_{11}/k_B = 36.4$ K, $b_{11} = 3.43$ Å, $\alpha_{11} = 11.1$, $\epsilon_{12}/k_B = 15.5$ K, $b_{12} = 3.37$ Å, $\alpha_{12} = 12.7$, $\epsilon_{22}/k_B = 10.57$ K, $b_{22} = 2.97$ Å, $\alpha_{22} = 13.6$, 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 Rec 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

T (K)	V (cm ³ /mol)	x	Mixture	Equivalent pure fluids			
				Rec	(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

actly as before from consideration of the compressibility equations, this procedure leads to the MRs

$$(I) \quad \langle eb^3 \rangle, \langle eb^3 \alpha (\alpha - 7) / (\alpha - 6) \rangle$$

if the energy equation is used or

$$(II) \quad \langle eb^3 \alpha (\alpha - 7) / (\alpha - 6) \rangle, \langle eb^3 \alpha (\alpha^2 - 56) / (\alpha - 6) \rangle$$

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 the index (k) denotes the k th 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

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

and

$$g_x(r) = \bar{G}(\alpha_x r / b_x). \quad (12)$$

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

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

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 (table 1). 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 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.

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