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ONE- AND MULTI-COMPONENT THEORIES OF MIXTURES

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We describe one-component statistical mechanical theories and van der Waals's effective one-component mixture model. We then show how to apply them to mixtures (containing CO₂) to extract reliable unlike-pair potentials involving CO₂ molecules as well as their dissociation products. A more fundamental approach will require the development of a perturbation or variational theory of mixtures based on a non-additive hard-sphere mixture reference system. Recent progresses made in this direction by means of an integral equation and computer simulations is described.

INTRODUCTION

Main reasons for studying mixtures are: (i) real world is made of mixtures, but at present there is no reliable theory about them; (ii) some physical phenomena, such as fluid-fluid or solid-solid phase separation that can occur only in mixtures need to be understood; (iii) we are interested in finding intermolecular forces among dissimilar molecules.

PURE SYSTEMS

Understanding the behavior of pure systems is a prerequisite to understanding mixtures. The essential physics behind reliable current models for pure systems owes to van der Waals more than 100 years ago. Van der Waals's idea is that a harsh repulsive portion, rather than the long-range portion, of an intermolecular potential controls thermodynamics and structural properties of condensed phases. Five ingredients are needed to formulate van der Waals's idea into a mathematically rigorous framework:

- (a) an optimum way to break an intermolecular potential $V(r)$ into a hard-sphere-like interaction $V_0(r)$ and a perturbation term $W(r)$,

$$V(r) = V_0(r) + W(r), \quad (1)$$

- (b) a specific expression for $V_0(r)$ and $W(r)$,

- (c) an expression for the Helmholtz free energy A ,

$$A = A_0 + A_1, \quad (2)$$

in terms of the Helmholtz free energy A_0 for the reference system and that (A_1) for the perturbation potential,

- (d) an expression for the hard-sphere (HS) diameter to represent the reference potential,
(e) convenient expressions for the HS equation of state (EOS) and radial distribution function $g^{HS}(r)$.

Specific expressions needed for items (a) - (e) are available for classical fluids.¹⁻³ One approach is to use our perturbation theory (PT)¹ which extends earlier theories² to high pressure. The second approach is to employ a variational theory (VAR) developed by Ross.³ Both give about equally reliable results and have been successfully extended to describe solid-phase thermodynamic properties,^{4,5} using analytic expressions⁶ for $g^{HS}(r)$. As an example, Table 1 compares PV/NkT (P = pressure, V = volume, T = temperature; $\rho = N/V$) data based on the PT and Monte Carlo (MC) simulation data for an exponential-6 (exp-6) potential,

$$V(r) = \frac{\epsilon}{(\alpha - 6)} \{ 6 \exp[\alpha(1 - r/r^*)] - \alpha(r^*/r)^6 \}, \quad (3)$$

where parameters, α , ϵ , and r^* are specific to each chemical species and can be obtained from experimental data. It is noteworthy that PT is about equally reliable as MC (within MC's statistical errors). Yet, its computation time takes several orders of magnitude less than those required for MC.

Table 1. PV/NkT for an exp-6 potential ($\alpha = 13$).

$\rho(r^*)^3 / \sqrt{2}$	Monte Carlo	PT
0.9	3.27	3.27
1.0	3.81	3.80
1.5	8.08	8.04
2.05	16.58	16.65

EFFECTIVE ONE-COMPONENT MIXTURE MODEL

Compared to like-pair potentials described above, the exp-6 parameters for unlike-pairs are experimentally less well known. But they can be expressed as

$$\begin{aligned} r_{ij}^* &= k_{ij}(r_{ii}^* + r_{jj}^*) / 2, \\ \epsilon_{ij} &= l_{ij} \sqrt{\epsilon_{ii} \epsilon_{jj}}, \\ \alpha_{ij} &= m_{ij} \sqrt{\alpha_{ii} \alpha_{jj}}, \end{aligned} \quad (4)$$

in terms of like-pair parameters ($r_{ii}^*, \epsilon_{ii}, \alpha_{ii}$) and small multiplicative constants (k_{ij}, l_{ij}, m_{ij}) which can be fixed if appropriate theoretical or experimental data are available. Otherwise, we set $k_{ij} = l_{ij} = m_{ij} = 1$ which is commonly referred to as the Lorentz-Berthelot rule.

We assume mixtures of chemical species i and j , interacting with exp-6 potentials [Eqs. (3) and (4)] to be a *hypothetical one-component* system interacting with a composition (x_i)-dependent exp-6 parameters,⁷

$$\begin{aligned} (r^*)^3 &= \sum_{i \geq j \geq 1}^n x_i x_j (r_{ij}^*)^3, \\ (\epsilon)^3 &= \sum_{i \geq j \geq 1}^n x_i x_j \epsilon_{ij} (r_{ij}^*)^3 / (r^*)^3, \\ (\alpha)^3 &= \sum_{i \geq j \geq 1}^n x_i x_j \epsilon_{ij} \alpha_{ij} (r_{ij}^*)^3 / \epsilon (r^*)^3. \end{aligned} \quad (5)$$

The fact that one-component calculations are much simpler than mixture calculations provides a reasonable justification for using this so-called improved van der Waals one-fluid model. In fact, comparisons with two-component MC for He-H₂ mixtures in Table 2 shows that the effective one-component model (using VAR) produces excellent results at high pressure and temperature.

Table 2. Pressure (GPa) of an equimolar mixture of H₂ and He.

T (K)	V (cm ³ /mol)	2-component Monte Carlo	Effective 1- component theory
50	20	0.047±0.01	0.05
100	14	0.338±0.008	0.35
300	10	1.856±0.02	1.91
4000	8	12.43±0.2	12.6
7000	4.5	54±1	55.3

APPLICATION TO SHOCK DISSOCIATION OF CO₂

Motivations behind studying unlike-pair interactions in condensed phases are: (a) these data are unavailable; (b) they can, however, be extracted from strong shock wave data showing shock-induced chemistry; (c) one can study a fluid phase separation at high P & T as recently done for N₂ + H₂O mixtures.⁸ As an example, we show below how to extract unlike-pair interactions from the recent shock data⁹ of liquid CO₂.

A strong shock forces CO₂ molecules to partially dissociate into O, O₂, CO, and carbon residues in the graphitic, diamond, or liquid phase. We assume these dissociation products and CO₂ to establish a chemical equilibrium. Their chemical concentrations $\{n_i\}$ will change with T and P and have to be determined by minimizing the Gibbs free energy $G(P, T, \{n_i\})$,

$$G(P, T, \{n_i\}) = \sum_i n_i \mu_i, \quad (6)$$

with respect to $\{n_i\}$. The connection between the statistical mechanical theories discussed above (including interaction potentials $V_{ij}(r)$) and $G(P, T, \{n_i\})$ occurs strictly through the chemical potentials μ_i . The minimization is done using the CHEQ code,¹⁰ which evaluates μ_i using the variational theory and the effective one-component mixture model.

For this purpose, we need to know interactions of dissociation products involving single elements (O-O, CO₂-O, O₂-O₂), molecule-molecule interactions (CO-CO, CO₂-CO₂, CO₂-O₂, O₂-CO), and molecule-atom and atom-atom interactions (CO-O, CO₂-O). Among these nine interactions, only three like-pair interactions (O₂-O₂, CO-CO, CO₂-CO₂) are directly determinable from experiment based on one-component systems. The rest have to be determined by adjusting (k_{ij}, l_{ij}, m_{ij}) parameters in Eq. (4) to fit the shock data of liquid CO₂. Figure 1 shows the Hugoniot of liquid CO₂ obtained by adjusting the interactions parameters described above. They are compared with the experimental data.⁹ As shock pressures increase, CO₂ will dissociate into CO and O species. At pressures above 40 GPa, our calculation predicts that a significant proportion of carbon atoms will condense into the liquid phase,

It gives raise to a shoulder-like structure seen in the experimental data near 40 GPa. The same set of interaction parameters also gives a satisfactory

Fig. 1. Theoretical and experimental Hugoniot of liquid CO₂

Hugoniot for liquid CO₂.¹¹ Such an additional test provides a strong self-consistency criterion for unlike-pair potentials determined in this manner.

IMPROVED MIXTURE MODEL

The next generation mixture model requires replacement of the effective one-component approximation, Eq. (5), by a multi-component mixture model. To do this, we need items (a) to (e) (described earlier for pure systems) for mixtures. One major bottleneck in this long-range research project is item (e), i.e., lack of convenient expressions for the HS mixture EOS and the HS mixture radial distribution function $g_{ij}^{HS}(r)$. The former is needed to represent the reference system and the latter for evaluation of the perturbation correction A_1 and also the HS diameter d_{ij} .

There are a large number of independent variables to consider for the HS mixture EOS, i.e., density ρ , both like- ($i=j$), and unlike- ($i \neq j$) pair HS diameters defined by $\{d_{ij} = (d_{ii} + d_{jj})(1 + \alpha_{ij})/2\}$, and species composition $\{x_i\}$. The use of non-zero nonadditivity parameters $\{\alpha_{ij}\}$ is closer to nature and is needed to describe compound forming alloys or phase separations.

The EOS of pure HS is satisfactorily described by the Carnahan-Starling expression,¹² and that for the additive HS (AHS) mixtures by the Mansoori-Carnahan-Starling-Leland form.¹³ Our goal is to obtain a similar expression for nonadditive HS (NAHS) mixtures. One cost-effective way to do so is to use the modified Martynov-Sarkisov (MMS) integral equation for $g_{ij}^{HS}(r)$ developed by Ballone *et al.*¹⁴ They have shown that MMS agrees closely with

MC data for NAHS. Hence, our approach is to generate EOS data with MMS over a large range of $\{\eta_{ij}, \alpha_{ij}, x_i\}$ and find an expression which fits these data. After this is done, we can try to use the same expression to fit computationally more demanding MC data for NAHS systems at sparsely separated values of $\{\eta_{ij}, \alpha_{ij}, x_i\}$.

Table 3 gives PV/NkT obtained using MMS and our preliminary fit¹⁵ based on an extension of the expression [Eq. (2.6) in Ref. 14] by Ballone *et al.* for symmetric HS mixtures ($d_{11} = d_{22}, x_1 = x_2$). Both lie within 1 % of each other. Further refinement of this work to nonsymmetric case $x_1 \neq x_2$ using MC data on NAHS is in progress and will be reported in due course.¹⁵

Table 3. PV/NkT for symmetric HS mixtures $d_{11} = d_{22} = d, x_1 = x_2$.

α	ρd^3	Fit ^a	MMS ^b	%-error
0.05	0.1	1.261	1.262	-0.08
0.05	0.5	3.592	3.593	-0.03
0.02	0.1	1.248	1.249	-0.08
0.02	0.7	6.083	6.059	0.39
-0.2	0.2	1.384	1.384	0.00
-0.2	1.2	8.174	8.119	0.67
-0.5	0.4	1.616	1.615	0.06
-0.5	1.6	8.045	8.060	-0.19

^a Fit = least-squares fit to MMS based on a modification of Eq. (2.6) in Ref. 14.

^b MMS = modified Martynov-Sarkisov equation [Ref. 14].

CONCLUDING REMARKS

We have described the one-component effective mixture model and how one can use it to extract unlike-pair potentials in condensed phases. We plan to remove the effective one-component mixture model by a more basic mixture model. One key area in this regard is to obtain a reliable analytic expression for a reference system, i.e., non-additive hard-sphere mixtures. We have developed such an expression for an equal-diameter symmetric case using the MMS integral equation. Our next plan is to extend it to cases with unequal-diameter nonsymmetric cases and to investigate a possible fluid phase separation, all using MC data for NAHS. After this is done, we will be in a strong position to build a truly basic mixture theory.

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