THE EFFECT OF CROSS INTERACTIONS ON MIXING PROPERTIES: NON-LORENTZ–BERTHELOT LENNARD-JONES MIXTURES

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Dedicated to Professor William R. Smith on the occasion of his 65th birthday.

Binary mixtures of two identical Lennard-Jones fluids with non-Lorentz–Berthelot combining rules have been simulated at ambient-like conditions in order to examine the effect of cross interactions on mixing properties – excess volumes and enthalpies. Various combinations of deviations of both energy and size cross parameters from the Lorentz–Berthelot rules have been considered. Whereas consequences of the deviations for excess volume are rather straightforward, a variety of behavior types is found for excess enthalpy, including an excess function with three extrema.

Keywords: Binary mixtures; Lennard–Jones fluids; Non-Lorentz–Berthelot rules.

Intermolecular potential functions of various complexity are developed by adjusting parameters of an appropriate function to pure fluid experimental data. Advances in computer technology and quantum chemistry have made it possible to consider rather complex functions and achieve a very good agreement with experiment for a large number of fluids, ranging from nonpolar fluids such as hydrocarbons to such complex fluids as associating ones. However, this applies only to pure fluids and in no way to mixtures. We are not aware of any attempt to develop a potential model for a heterogeneous dimer, i.e., for an interaction between two different molecules and its subsequent application to a dense bulk phase. Molecular modeling of mixtures relies thus on the accurate pure fluid models and purely empirical combining rules which are, however, incongruent with the physical nature of pure fluid effective potentials. Furthermore, the properties of mixtures

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are known to be very sensitive primarily to the cross interaction, which means that even a very small change may produce a very large effect. Consequently, the results obtained using this approach are usually unpredictable.

Typical binary mixtures for which the failure of the accurate pure fluid pair potential models to reproduce at least qualitatively the properties of the mixture is conspicuous are aqueous solutions of lower alcohols. It turns out that realistic potential models (e.g., TIP4P for water and OPLS for methanol) are able to reproduce reasonably well only the excess volume, to some extent qualitatively also the excess enthalpy, but seem to fail to reproduce, even qualitatively, the composition dependence of the partial molar volume of methanol at its low concentrations (see, e.g., refs[1,2] and references therein). Effective pair potentials developed for pure fluids seem thus to have their limits as regards their application to mixtures with specific interactions and further investigations are therefore highly demanded; particularly, basic investigations on the cross interactions.

The used cross interactions may be augmented in a number of ways, e.g., by introducing nonadditivity of interactions. However, before embarking on such a complex project it seems more instructive to retain the pairwise additivity and examine first the effect of deviations from the common combining rules.

The most common combining rules are those of Lorentz–Berthelot (LB) which set the cross dimension parameter to the arithmetic mean of those of the pure components, and the cross energetic parameter to their geometric mean[3]. Some time ago Duh et al.[4] studied effects of deviations of the cross interactions from those given by the LB rules for a supercritical mixture of two identical Lennard-Jones (LJ) fluids considering in simulations only two compositions and only one set of cross parameters. As a first step in an ongoing project on complex mixtures we adopt in this paper the same approach, i.e., we consider the same LJ mixture but at a typical liquid condition and perform extensive molecular simulations for a large set of cross parameters and the entire composition range. It is found that deviations from the LB rules may give rise to qualitatively different behavior of excess functions.

BASIC DEFINITIONS AND COMPUTATIONAL DETAILS

Standard NPT Monte Carlo (MC) simulations[5] on binary mixtures of the LJ fluids

$$u_{ij}(\mathrm{r}_{ij}) = 4\varepsilon_{ij}\left[\left(\frac{\sigma_{ij}}{r_{ij}}\right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}}\right)^{6}\right] \tag{1}$$

were performed. Both components of the mixture were identical

$$\sigma_{11} = \sigma_{22} \equiv \sigma; \quad \varepsilon_{11} = \varepsilon_{22} \equiv \varepsilon \tag{2}$$

but the cross interactions were varied in order to find out how they affect the thermodynamic properties of the mixture; in particular, the excess mixing properties. The cross interaction parameters, σ_{12} and ε_{12}, are given by

$$\sigma_{12} = \frac{1}{2}(1+\delta_\sigma)(\sigma_{11}+\sigma_{22}) \equiv (1+\delta_\sigma)\sigma \tag{3}$$

and

$$\varepsilon_{12} = (1+\delta_\varepsilon)(\varepsilon_{11}\varepsilon_{22})^{\frac{1}{2}} \equiv (1+\delta_\varepsilon)\varepsilon\ . \tag{4}$$

If both δ_σ and δ_ε are set to zero, the LB rule is recovered. The size and energy parameters, σ and ε, are used to scale distances and energies, respectively, and we use thus dimensionless quantities henceforth, $\rho \leftrightarrow \rho\sigma^3$, $T \leftrightarrow k_\mathrm{B}T/\varepsilon$, and $P \leftrightarrow P\sigma^3/\varepsilon$, where ρ is the number density and k_B is the Boltzmann constant.

The studied systems consisted of $N = 1372$ particles in a cubic simulation box. The LJ potential cutoff was set to 5σ and a simple non-shifted cut-potential was used. Every MC step consisted of $3N$ attempted displacements followed by one attempt to change the volume of the system. Simulation parameters were set so as to maintain, approximately, the acceptance ratio of the displacements about 0.3 and that of the volume about 0.5. Both negative and positive values of δ_ε and δ_σ were considered for concentrations covering the range (0,1). To keep the development of the system during simulations under control, various control quantities were monitored[6].

A typical mixture property from which further quantities may be derived is the excess property X of mixing defined, in general, by

$$\Delta X = X_{\mathrm{mix}}(P,T) - \sum n_i X_i^{(0)}(P,T) \tag{5}$$

where X_{mix} is the total measured property of the mixture, $X_i^{(0)}$ is the molar property of pure compound i (at the same (P,T)), and n_i is the number of moles of component i. In the case of the considered LJ mixture we get

$$\Delta X = X_{\mathrm{mix}}(P,T) - X_{\mathrm{LJ}}(P,T)\,. \tag{6}$$

Whereas the total volume is obtained directly during the simulation, dimensionless residual enthalpy per molecule, $h \leftrightarrow H/\varepsilon N$, is evaluated from the relation

$$\frac{h}{T} = \frac{u}{T} + \frac{P}{\rho T} - 1 \tag{7}$$

where u is the internal residual energy per molecule.

RESULTS AND DISCUSSION

The considered LJ mixture was studied at a temperature close to the triple point, T = 0.7, and pressure P = 0.0017, i.e., at the thermodynamic state that corresponds, approximately, to ambient-like conditions (Fig. 1). Concentrations covered the range from x = 0.0 to 0.5 (because of symmetry of the mixture, the results for the other half of the range are identical), where

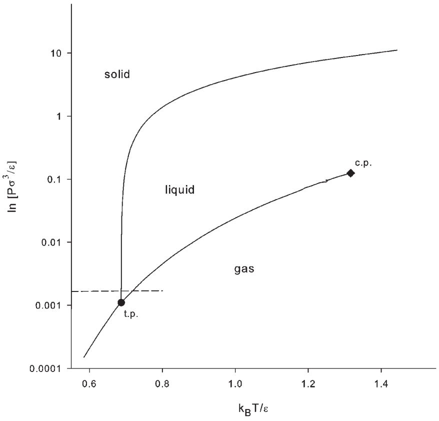

FIG. 1
Phase diagram of the pure LJ fluid. The dashed line indicates the pressure considered in this paper, c.p. and t.p. denote the critical and triple points, respectively

x is the mole fraction, $x_i = n_i/(n_1 + n_2)$. Depending on the chosen values of δ_σ and δ_ε, two types of mixtures were considered: (i) one with $\delta_\sigma = 0$ and a number of δ_ε, $\delta_\varepsilon = \{\pm 0.25, \pm 0.20, \pm 0.15, \pm 0.10, \pm 0.05\}$; this choice is considered with respect to potential future applications in which the cross energy plays a predominant role (e.g., aqueous solutions of alcohols) and (ii) all four combinations of non-zero deviations, $\delta_\varepsilon = \pm 0.2$ and $\delta_\sigma = \pm 0.2$.

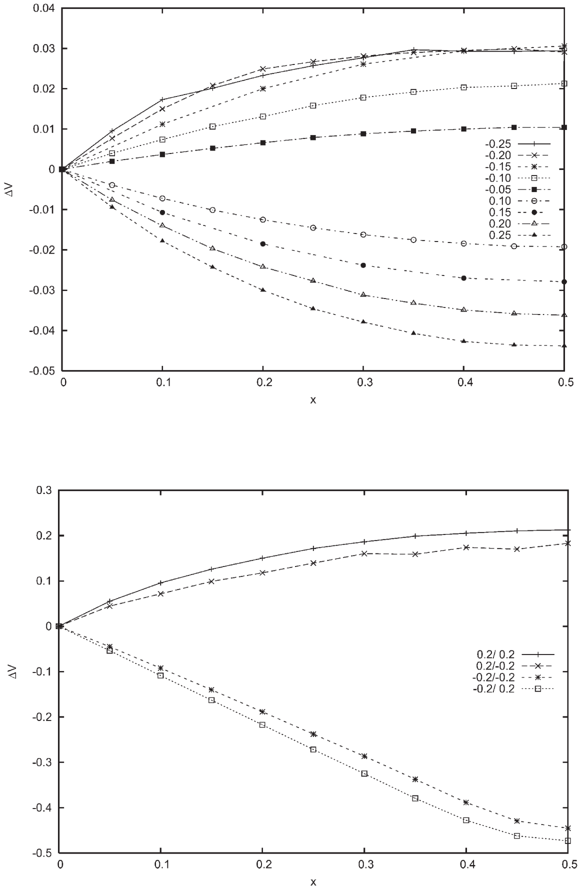

FIG. 2
Excess volume for $\delta_\sigma = 0$ and different values of δ_ε (upper graph), and for a combination of non-zero values of δ_σ and δ_ε (lower graph), denoted as $\delta_\sigma/\delta_\varepsilon$

The excess volumes of mixing are shown in Fig. 2, and excess enthalpies in Fig. 3. As one can see, in the case of $\delta_\sigma = 0$, both negative and positive values of δ_ε produce, qualitatively, the same effect for both the excess volume and enthalpy, with deviations a bit more pronounced for positive δ_ε. This is particularly evident for enthalpy; in this case ΔH is considerably smaller (in the absolute value) for negative δ_ε, and a further decrease of δ_ε does not cause a further uniform deviation. In general, positive values of δ_ε give negative excess properties and vice versa.

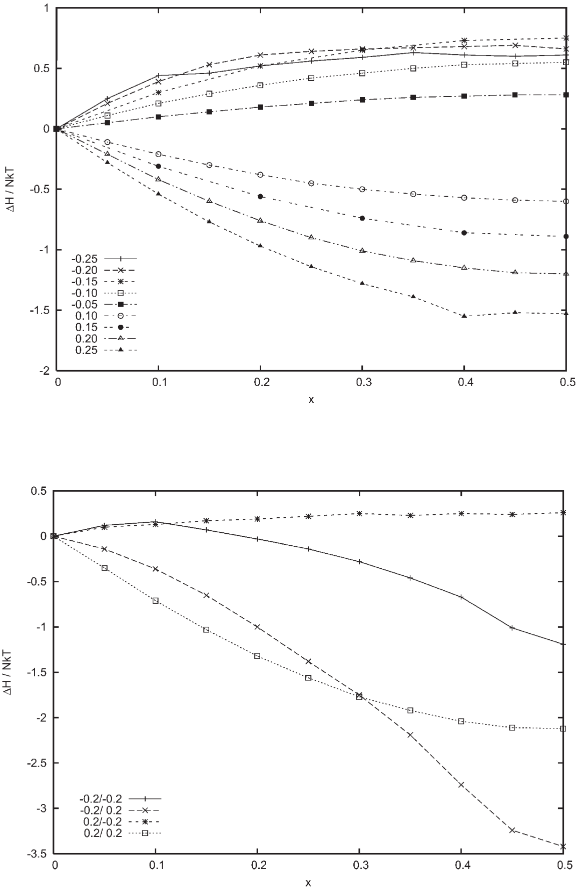

FIG. 3

The same as Fig. 2 for excess enthalpy

In the case of combined deviations from the LB rule, the situation seems rather simple for the excess volume. The sign of ΔV is determined, as one could expect, by the sign of δ_σ: negative δ_σ yields negative ΔV, and positive δ_σ positive ΔV. Differences caused then by different δ_ε do not seem to be significant. Nonetheless, one striking feature, with respect to consequences, is a nearly linear dependence of ΔV for negative δ_σ: it implies that the partial molar volume may exhibit rather unusual Heaviside function-like behavior. The situation is much more complex for the excess enthalpy. At low concentrations the sign of ΔH follows the same trend as in the case of $\delta_\sigma = 0$. However, at higher concentrations the effect of δ_σ begins to compete and the composition dependence becomes more complex. For negative δ_ε, the effect of δ_σ may even prevail causing ΔH to pass through a maximum and then to become negative. As a result, we get excess enthalpy with three extrema (over the entire composition range), the well-known feature observed experimentally, e.g., for the benzonitrile–toluene mixture[3]. Another interesting behavior we observe for $\delta_\sigma/\delta_\varepsilon = (-0.2/0.2)$. As we see, in this case the curve changes its curvature which means that its derivative (i.e., partial molar quantity) should exhibit a minimum.

With respect to the above findings, particularly for the combined deviations, one may ask a question whether they are not an artefact of the simulations. The considered state point lies rather close to the triple point and large deviations from the LB rule may give rise to demixing. No such phenomenon was however observed and the monitored control quantities indicated that the sample represented a homogeneous equilibrium phase.

CONCLUSIONS

In this note, which should be viewed as a feasibility study, we have investigated various Lennard-Jones mixtures with cross interaction parameters different from those given by the Lorentz–Berthelot rule in order to find out the effect of the cross interactions on the concentration behavior of excess functions. It turns out that by varying the cross parameters, a spectrum of the properties of excess functions can be obtained, including those observed for mixtures of complex compounds. The finding may thus help to understand the behavior of mixtures and to develop combining rules for different classes of mixtures. Further investigations along this line seem therefore highly desirable; they should include not only a larger range of values of δ_σ and δ_ε and other state points outside the dense liquid conditions, but other quantities as well. Specifically, partial molar quantities are of great importance but their evaluation requires much more accurate (i.e., longer runs) excess properties or even another technique.

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