COMMENTS

Comment on: Rectilinear diameters and extended corresponding states theory

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In a recent paper,[1] Singh and Pitzer (SP) show that existing data for the slope of the coexistence curve diameter and the critical compressibility factor for several fluids show a linear dependence on Pitzer's acentric factor ω.[2] They compare their results to earlier work by Goldstein *et al.*[3,4] and Pestak *et al.*[5] in which trends in these properties were shown to be due to changes in the relative importance of three-body interactions in the fluids. We will refer to Refs. 3–5 collectively as GP. SP conclude, in contradiction with the results of GP, that these properties do not depend systematically on the relative strength of three-body forces, but rather are due to "the shape of the two-body potential as indicated by the acentric factor." In this comment we argue that the empirical parameter ω in fact implicitly depends upon many-body interactions, and that as a result the microscopic origin of the observed correlation of the diameter slope and other properties with ω cannot be attributed to two-body effects alone.

The coexistence curve diameter is $\rho_d = (\rho_l + \rho_v)/2\rho_c$, where ρ_l and ρ_v are the densities of the coexisting liquid and vapor phases below the critical point of a fluid and ρ_c is the critical density. Far from the critical point the diameter is linear in temperature with a slope symbolized by A_1.

The acentric factor ω is a parameter commonly used to characterize the departures of fluids from the principle of corresponding states.[2] It is often said to be a measure of the departure from spherical symmetry of the molecules, and hence of the two-body intermolecular interactions, in the fluid under consideration. ω is not a microscopic quantity. Rather, it is determined empirically from experimental data: It is defined in terms of the slope of the vapor pressure curve at a reduced temperature $T/T_c = 0.7$. Thus, ω is defined purely in terms of ensemble averages (i.e., thermodynamic observables); there is no microscopic component to its definition.

Three-body interactions are present in any real fluid; in fact it is known that in dense fluids they contribute on the order of 10% to the cohesive energies.[6] The slope of the vapor pressure curve of a fluid is obviously a function of the interactions between the fluid molecules. Thus the parameter ω as defined above must implicitly depend on the three-body interactions in the fluid, and indeed on any microscopic effects that contribute to the fluid properties. Saying that ω parametrizes *only* the departures from sphericity of the two-body potential may be useful conceptually, but is clearly an approximation to the true state of affairs and cannot rigorously be true. The observed correlations between A_1 and the critical compressibility $z_c = P_c/\rho_c k_B T_c$, and ω cannot therefore be attributed only to changes in the two-body potential. The fact that correlations exist is not in itself surprising and could in fact be predicted by general thermodynamic arguments.[7] A_1 and ω are, after all, both thermodynamic quantities arising from the same underlying statistical mechanical principles. That the correlations are as simple as those demonstrated by SP is interesting and merits theoretical study.

A similar argument could be made concerning the observed correlation between ω and the second virial coefficient. This correlation simply reflects the fact that the slope of the vapor pressure curve depends on two-body interactions. It does *not* rule out any dependence of ω on other factors, including three-body effects.

In GP it was shown that the ratio of the strength of three-body dispersion forces of the Axilrod–Teller type to that of two-body forces is given by the dimensionless product $\alpha_p\rho_c$, where α_p is the molecular polarizability. By a simple mean-field calculation GP showed that A_1 should increase linearly and that z_c should decrease linearly with $\alpha_p\rho_c$. The ratio of the slopes of these two functions should be a constant of order -10. Experimental data analyzed in GP confirmed these predictions. In contrast to ω, $\alpha_p\rho_c$ *is* a fundamental property of the fluid. α is a microscopic property with a direct correspondence to terms in the Hamiltonian. ρ_c provides a natural length scale for the system. In a first-order perturbation theoretical treatment of many-body interactions in fluids, the critical density of the corresponding fluid with only two-body interactions enters the problem naturally; our use of measured values of ρ_c is simply a matter of convenience. The theory of GP thus suggests a microscopic theoretical explanation for the observed trends in A_1 and z_c rather than just a parametrization of the data.

The theory of GP does not attempt to treat the fine details of the intermolecular interactions and the agreement between that theory and the experimental results would presumably be perfect only for a set of fluids in which the forms of the two- and three-body interactions were identical. The fluids studied in GP (Ne, N_2, C_2H_4, C_2H_6, and SF_6) all have more or less spherical molecules, and one would therefore expect the nature of the two- and three-body forces in these fluids to be similar. Figure 3 of SP shows that the *n*-alkanes show deviations, increasing systematically with the molecular length, from the relationship determined for the fluids treated in GP. In fact these deviations are not large in the spirit of GP's simple mean-field calculation, but they can be easily explained as being due to the changing shape of the molecules, which influences the intermolecular interactions in a way that is not included in that calculation. These effects are implicitly accounted for in the determination of ω, thus the better fit of the data to a straight line when they are plotted against ω in SP. This does not indicate, as SP imply, that the general increase in A_1 with $\alpha_p \rho_c$ is not due to an increase of the relative importance of three-body effects, only that real fluids have more complicated potentials than treated by GP. It does demonstrate that ω is more useful than $\alpha_p \rho_c$ as a parameter for the correlation of fluid properties; that is exactly what ω was designed to be. Similar systematic deviations, but in the opposite sense, are observed in the data for z_c, as seen in Fig. 4 of SP. GP predict that the slopes of these two quantities should have a constant ratio; the directions of these deviations are consistent with this prediction.

The good correlation between A_1 and ω and between z_c and ω presented by SP is perhaps useful, but since ω is a function of many microscopic variables the physical insight gained from this result is small. SP state that the parametrizations of fluid properties involving ω give "correct values for...dense fluids where three-body forces are present" and that therefore the relative role of three-body interactions cannot vary a great deal among different fluids. This reasoning neglects the implicit dependence of ω on factors other than the shape of the molecules. In fact Fig. 1 of SP may simply illustrate a tautology: It is quite possible that the slope of the vapor pressure curve, and hence ω, depends on three-body effects in exactly the same way as does the slope of the coexistence curve diameter. A mean-field calculation of this quantity, in the spirit of GP, would clarify this issue. In the absence of such a calculation, SP's conclusion that the trends in the coexistence curve diameter slope and other near-critical properties are due to "the shape of the two-body potential" and not to changes in the relative importance of three-body interactions is unjustified. The work of GP presents strong evidence that three-body interactions are the microscopic origin of the observed trends, and of the nonanalytic behavior of the diameter near the critical point. The acentric factor ω provides a useful way of parametrizing fluid properties, but its use masks the underlying physics.

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