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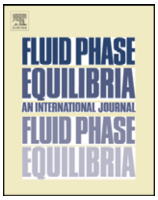

Mean-field theoretical analysis of the corresponding-states behavior of model fluids with variable interaction range

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ABSTRACT

In a recent communication [Fluid Phase Equilib. 272 (2008) 93–95], Duda and Orea suggested the existence of remarkably simple relationships among the critical parameters of several model fluids with variable interaction range. In addition, they introduced a new way of scaling supercritical pressure–volume–temperature (*PVT*) data for a pure substance in a corresponding-states representation. Using different mean-field theories for the square-well fluid and the Yukawa fluid, we investigate whether these approximate equations of state adhere to the new criteria formulated by Duda and Orea. It is found that most theories indeed predict the suggested simple linear relationships between the critical pressure and the critical temperature as well as between the critical density and the reciprocal of the critical temperature for long interaction ranges, but deviations from these simple rules occur for short interaction ranges. Some of the theories, however, indicate that the dependence of the critical density on the interaction range might be more complicated for the square-well fluid. The revised scaling concept of representing the reduced pressure P/P_c at a given reduced temperature T/T_c as a function of the newly defined reduced density $\rho\sigma/\rho_c^{2/3}$, where σ denotes the diameter of a particle, does indeed lead to a better agreement of the data for different interaction ranges than the conventional scaling in terms of ρ/ρ_c for both model fluids studied here.

1. Introduction

Recent simulations of several model fluids with variable interaction range have led Duda and Orea [1,2] to proposing a revision of the way the density is scaled when applying a long-standing principle in thermodynamics: the law of corresponding states. This principle offers a unified description of the behavior of pure fluids and was first formulated by van der Waals within the framework of his famous equation of state [3–5]:

$$P = \frac{\rho kT}{1-\rho b} - a\rho^2, \tag{1}$$

where P denotes the pressure, T the absolute temperature, and ρ the number density, while a and b are the cohesion parameter and the excluded volume, respectively; k is Boltzmann's constant. By scaling the state variables P, T, and ρ (or, equivalently, the molar volume V) by their respective critical values, P_c, T_c, and ρ_c, van der Waals obtained an equation of state in terms of the reduced variables $P_R = P/P_c$, $T_R = T/T_c$ and $\rho_R = \rho/\rho_c$, which would be universally applicable if all pure substances obeyed the van der Waals equation:

$$P_R = \frac{8\rho_R T_R}{3-\rho_R} - 3\rho_R^2. \tag{2}$$

The individual properties of any of these (hypothetical) substances, which are described by only two parameters, a and b, within the van der Waals equation of state, are accounted for by the specific critical parameters of the respective fluid. While the van der Waals equation of state is not particularly accurate for any real or model fluid, it is qualitatively correct in many respects (with the exception of the fluid's critical behavior due to the mean-field character of the van der Waals equation). In particular, it can be shown [6] that the behavior of simple fluids whose pair interaction potential is spherically symmetric, of sufficiently short range and which depends on only two parameters adheres to a corresponding-states law as conceived by van der Waals, even if these fluids do not obey his equation of state exactly. These two parameters determine the interaction potential u acting between two molecules of the fluid by setting the characteristic energy scale ϵ and the length scale σ of this interaction. The molecular properties ϵ and σ play the role of the van der Waals parameters a and b on the microscopic scale, even if the fluid behavior is not accurately described by the van der Waals equation. For a hypothetical van der Waals fluid composed of attractive hard-sphere particles, these parameters are interrelated by $a = -2\pi\int_\sigma^\infty r^2 u(r)\mathrm{d}r$ and $b = 2\pi\sigma^3/3$, where $u(r)$ denotes

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the attractive pair potential and r the interparticle distance [6,7]; the energy scale ϵ is then set by the energy of two particles at contact, $u(\sigma)$. The numerical value of a depends, of course, on the exact details of the function $u(r)$, not only on its value at contact, $u(\sigma)$, which determine ϵ.

A generalized principle of the corresponding-states idea, independent of any specific equation of state, was formulated and tested by Guggenheim [8]. In addition to the pressure as a function of temperature and density, he found other properties, such as the surface tension, the second virial coefficient and the liquid–vapor coexistence curve, to follow a corresponding-states law as well when expressed in suitably reduced units. These laws are particularly well obeyed by simple nonpolar substances, such as noble gases, oxygen, and nitrogen, but deviations are seen for strongly dipolar substances, especially for those whose molecules are able to form hydrogen bonds [9]. As already Guggenheim remarked in his article [8], these cases should not simply be regarded as failures of the corresponding-states principle, but rather as opportunities to learn more about the behavior of complex fluids.

As mentioned above, the law of corresponding states can be shown to hold rigorously for families of fluids for which the interaction potential is spherically symmetric, of sufficiently short range and characterized by only two parameters [6], one of which sets the energy scale, the other one the characteristic length scale of the fluid model. The Lennard–Jones potential is a famous example of such a potential:

$$u = 4\epsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right]. \tag{3}$$

Deviations from the corresponding-states principle formulated above must, however, already be expected for fluids which, while retaining the spherical symmetry of the pair interaction potential, require a third parameter – l, say – to specify the range of these interactions. Prominent examples of simple fluids with variable interaction range are the square-well fluid and the Yukawa fluid, which are the subject of this article (cf. Section 2). Less frequently studied model fluids in the context of varying interaction range include the Sutherland fluid and the Mie fluid.

When the respective interaction-range parameter of any of the above-mentioned model fluids is changed, the simple corresponding-states idea that $P_R = f(T_R, \rho_R)$ is represented by a complicated, but universal function f which is independent of the interaction range, is expected to break down [6]. Although the critical parameters (P_c, T_c, and ρ_c and, therefore, also the critical compressibility factor Z_c) depend on the interaction-range parameter as well, these variations are, in general, insufficient to scale out the range dependence of P_R, which should then be denoted as $P_R(T_R, \rho_R; l)$. Questions that arise in this context are (a) how severely will the deviations of $P_R(T_R, \rho_R)$ from a universal corresponding-states behavior be if the conventional density scaling is used and the interaction-range parameter is varied and (b) is there a way of revising the conventional density-scaling approach in such a way that the principle of corresponding states remains universally applicable?

Analyzing their recent simulation results for the Yukawa, Mie, and Sutherland fluids, Duda and Orea [1,2,10] suggested that a scaling of the density according to $\rho_r = \rho\sigma/\rho_c^{2/3}$ leads to a significantly improved collapse of the pressure data $P_R(T_R, \rho_r)$ of these fluids than the conventional density scaling does; the dependence on the interaction-range parameter is thus scaled out. No comparable simulation work has been carried out on the square-well fluid yet, but there are indications that it may be an exceptional case in the family of the above-mentioned simple model fluids with variable interaction range. The somewhat irregular behavior is suggested by the changes of the critical parameters found for the square-well fluid when the interaction range is varied. For the Mie, Yukawa, and Sutherland fluids, Duda and Orea [1,2,10] observed remarkably simple linear relationships between the critical temperature and the critical pressure as well as between the critical density and the reciprocal of the critical temperature. For the square-well fluid, however, especially the latter relationship seems to be more complicated [11]. In the above definition of the new reduced density variable $\rho_r = \rho\sigma/\rho_c^{2/3}$, the particle diameter σ is included to produce a dimensionless quantity; it represents the unit of length in the model fluid and has the advantage of being state-independent.

The aim of this study is to check if mean-field equations of state confirm the remarkable simulation results of Duda and Orea or if significant differences are seen. In addition, it is of interest to see how badly the conventional van der Waals scaling $P_R(T_R, \rho_R)$ fails for fluids of variable interaction range, both within mean-field theory and in simulations.

Due to the lack of sufficiently tested mean-field theories (equations of state) for the less frequently studied Sutherland and Mie fluids, we focus on the square-well and Yukawa fluids here, for which integral-equation studies, perturbation theories, and virial equations of state are available and have been sufficiently checked against computer simulations for us to be able to assess their range of validity [12].

The remainder of the paper is organized as follows: In Section 2, we introduce the model fluids and the respective theories used to describe their thermodynamic behavior. The results we obtained for the critical parameters as functions of the interaction-range parameter are compiled and analyzed in Section 3.1. Section 3.2 is dedicated to the application of the revised density-scaling approach of Duda and Orea, the performance of which with respect to the corresponding-states behavior of the pressure is compared to the conventional van der Waals scaling for the two model fluids. A brief summary of the most important findings is given in the concluding Section 4.

2. Model fluids and mean-field theories

The model fluids selected for a study of the influence of the interaction range on the critical parameters and on the corresponding-states behavior of the pressure in the different density-scaling approaches are the Yukawa fluid and the square-well fluid, which are particularly amendable to analytical theory. The piecewise constant square-well potential is by far the easiest to study theoretically because there is no explicit dependence of the pair interaction energy on the interparticle distance r. It may, in fact, be regarded as the simplest model fluid that displays liquid–vapor coexistence. In the Yukawa fluid, the attractive interactions decay exponentially (see below). This fluid model is often used to describe colloidal systems in which the Coulomb interactions among the particles are screened by counterions. The Debye screening length, which governs the exponential decay of the interaction potential in such systems, is determined by the ionic strength of the solution, its dielectric permittivity, and the temperature and is, therefore, state-dependent. In the Yukawa potential, however, this screening parameter is fixed.

2.1. Yukawa fluid

For this first model fluid with variable interaction range, the potential between two particles is defined by

$$u = \begin{cases} -\epsilon\dfrac{\exp[-\lambda(r-\sigma)/\sigma]}{r/\sigma}, & r \geq \sigma, \\ \infty, & r < \sigma, \end{cases} \tag{4}$$

where ϵ is the depth of the potential of the two particles at contact, and σ denotes their hard-sphere diameter, i.e., the distance