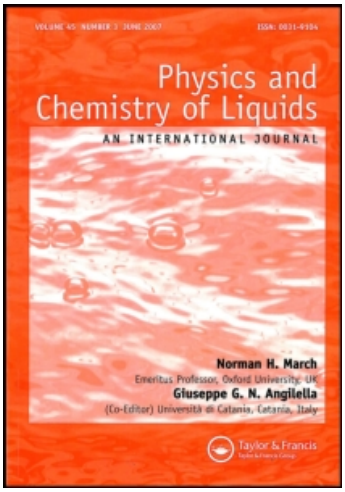

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Coexistence curves in monatomic fluids: the contrast between insulating argon and metallic assemblies

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LETTER

Coexistence curves in monatomic fluids: the contrast between insulating argon and metallic assemblies

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The recent study of Ashton *et al.* [D.J. Ashton, N.B. Wilding, and P. Sollich, J. Chem. Phys. **132**, 074111 (2010)], which is appropriate to insulating fluids like argon, is contrasted with the results for liquid metal assemblies, such as are discussed by Leys *et al.* [F.E. Leys, N.H. March, V.E. Van Doren, and G. Straub, Phys. Chem. Liq. **39**, 133 (2001)].

Keywords: liquid metals; coexistence curves

In earlier work, Leys *et al.* [1] (see also [2]) have proposed a modification of a semi-empirical treatment going back to Guggenheim [3], who studied the coexistence curves of a sequence of insulating fluids including argon, when dealing instead with the heavy alkali metals Rb and Cs. Here, we relate these studies to the recent article of Ashton *et al.* [4], which has motivated the present Letter.

Returning to Guggenheim's work [3], his figure 3.11 shows the reduced densities of coexisting liquid and vapour curves for the inert gases Ne, Ar, Kr and Xe, as well as for the molecular insulating fluids N_2, O_2, CO and CH_4. He notes first that if ρ^L denotes the density of the liquid and ρ^G that of the vapour in mutual equilibrium at temperature T, while ρ_c is the density at the critical point, then, following from the principle of corresponding states, one should anticipate that ρ^L/ρ_c and ρ^G/ρ_c should be common functions of T/T_c. How nearly this is the case for the eight insulating fluids listed above is clear from figure 3.11 in Guggenheim's book [3].

In fact, figure 3.11 contains curves obtained from his empirical formulae [3]

$$(\rho^L + \rho^G)/2\rho_c = 1 + \frac{3}{4}(1 - T/T_c), \tag{1}$$

and

$$(\rho^L - \rho^G)/\rho_c = \frac{7}{2}(1 - T/T_c)^{1/3}, \tag{2}$$

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which fit the eight insulating fluids above remarkably well. However, Leys *et al*. [1] have emphasised that Equations (1) and (2) do not work well for the metallic fluids Rb and Cs, and have proposed modifications to Equations (1) and (2) which read

$$(\rho^L + \rho^G)/2\rho_c = 1 + \text{const}(1 - T/T_c)^{2/3} \tag{3}$$

and

$$(\rho^L - \rho^G)/\rho_c = \text{const}'(1 - T/T_c)^{1/3}. \tag{4}$$

With this background, we turn next to [4], which will be briefly summarised below. In essence, these authors address the issue of how to determine the coexistence curve and the critical point parameters within the restricted Gibbs ensemble (RGE) [5,6]. In particular, in the subcritical region, in [4] an intersection method for estimating the coexistence densities has been proposed and tested. It involves measurements of the RGE peak densities as a function of the overall system density. In the near-critical regime, Ashton *et al*. [4] have described and extended, a finite-size scaling method by which accurate estimates of fluid critical point parameters can be obtained within the RGE.

However, in [4] it is also stressed that for single component fluids considered in this article, or mixtures of similarly sized particles, RGE simulations are not to be considered as competitive with standard ensembles such as the grand canonical ensemble, constant *NPT*, or the full Gibbs ensemble [7]. Ashton *et al*. [4] anticipate that their approach via the RGE will come into its own for highly size-asymmetric mixtures.

To conclude, we stress that in [4] the RGE is used only for a single-component fluid, which is described via a Lennard–Jones 6-12 potential. This limits the results to the Guggenheim plot in figure 3.11 of [3]. As emphasised in [1], while this plot is quite well fitted by Equations (1) and (2) cited above, appropriate for numerous insulating fluids, for liquid metal fluids typified by the heavy alkalis Rb and Cs these equations must be changed to the forms of Equations (3) and (4) cited above. Of course, these forms are, as stressed above, semi-empirical and it will clearly be of considerable interest for the future if finite scaling procedures such as applied in [4] to insulating fluids could be extended to treat metallic fluids. However, to date, accurate experimental data, to our present knowledge, is available only for fluid Hg, and the heavy alkalis Rb and Cs. A particular challenge for finite-size scaling is to explain the departures from the law of rectilinear diameters in the metallic fluids Rb and Cs.

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