Equation of state of sticky-hard-sphere fluids in the chemical-potential route

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The chemical potential of a fluid can be evaluated as the change in the Helmholtz free energy when a new particle is added to the system through a coupling parameter (ξ) which determines the strength of the interaction of the added particle to the rest of the system. This method provides the equation of the state (EOS) of the fluid in the so-called chemical-potential route (or μ-route). This can be considered as the fourth route in addition to the better known routes based on the pressure (or virial), compressibility, and energy equations. All these ways to obtain the EOS are *formally* equivalent.

In practice, the various thermodynamics routes have been mostly developed (under the assumption of additive pair interactions) using the so-called radial distribution function $g(r)$. Since all well-known theoretical methods to obtain $g(r)$ give approximate solutions, with the exception of a few, simple fluid models (for example, one-dimensional systems whose particles interact only with their nearest neighbors), the EOS obtained from different routes differ in general from one another.

The μ-route has been largely unexplored, except in the scaled-particle theory.[1] Recently, this method has been used to obtain a hitherto unknown EOS for the hard-sphere (HS) model in the Percus–Yevick (PY) approximation.[2] This method was then extended to multicomponent fluids for arbitrary dimensionality, interaction potential, and coupling protocol.[3] Its application to HS mixtures allowed us to provide a new EOS of this classical model in the PY approximation. Evidently, the μ-route represents a helpful tool for the construction of new EOS and the analysis of thermodynamic properties of fluids. It is therefore of great interest to consider its application to non-HS models.

In this paper we use the μ-route to evaluate the EOS of Baxter's sticky-hard-sphere (SHS) model. In this fluid, impenetrable particles of diameter σ interact through a square-well potential of infinite depth and vanishing width, characterized by a "stickiness" parameter α. The μ-route yields[4]

$$\beta\mu^{\mathrm{ex}} = -\ln(1-\eta) - 24\eta\int_{1/2}^{1} d\xi\, M(\eta,\xi), \tag{1}$$

$$M(\eta,\xi) \equiv \frac{\partial\left(\alpha_\xi - 1\right)\xi}{\partial\xi}\xi^2 y_\xi(\xi\sigma) + \frac{\alpha_\xi \xi}{\sigma}\left.\frac{\partial[r^2 y_\xi(r)]}{\partial r}\right|_{r=\xi\sigma}.$$

Here, η is the packing fraction and $y_\xi(r)$ is the cavity function of the added particle, which interacts with the rest of the particles via an SHS interaction of diameter $\xi\sigma$ and stickiness α_ξ.

By exploiting the exact knowledge of $y_\xi(r)$ within the PY approximation,[5] we have obtained the compressibility factor $Z \equiv p/\rho k_B T$ stemming from Eq. (1) with three different *protocols*: (A) $\alpha_\xi = (2\xi-1)^2\alpha$, (B) $\alpha_\xi = (2\xi-1)\alpha$, and (C) $\alpha_\xi = (2\xi-1)^{1/2}\alpha$. Not surprisingly, the resulting EOS depends on the protocol and differs from the one obtained from the virial (v), compressibility (c), or energy (e) routes.

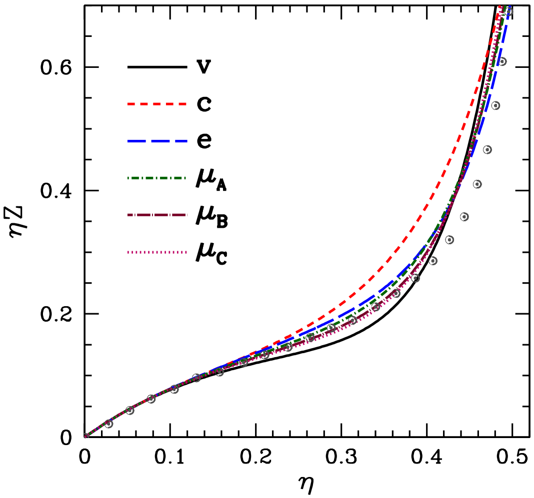

FIG. 1. Reduced pressure ηZ as a function of the packing fraction for and SHS fluid at $\alpha = \frac{5}{9} \simeq 0.556$. The curves correspond to PY results from various routes (as indicated on the plot), while open circles represent Monte Carlo calculations.[6]

As an illustration, Fig. 1 shows the density dependence of the reduced pressure ηZ at $\alpha = \frac{5}{9}$, as obtained from MC simulations and from the PY approximation via different routes. We can observe that the best performance in the region $0.15 \lesssim \eta \lesssim 0.4$ corresponds to the three versions of the μ-route, followed by the energy route. We have also obtained the vapor-liquid coexistence curve and observed that the best overall agreement with computer simulations[6] corresponds again to the μ-route.

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