Equation of state of polydisperse hard-disk mixtures in the high-density regime

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Recently, an approach to link the equation of state (EoS) of a monocomponent hard-sphere (HS) fluid to the EoS of a polydisperse HS mixture has been introduced [1, 2, 3, 4]. In this approach, the compressibility factor Z of the mixture may be expressed in terms of the one of the monocomponent HS fluid Z_p as

$$\phi Z(\phi) - \frac{\phi}{1-\phi} = \alpha\left[\phi_{\text{eff}} Z_p(\phi_{\text{eff}}) - \frac{\phi_{\text{eff}}}{1-\phi_{\text{eff}}}\right], \qquad (1)$$

where the effective packing fraction ϕ_{eff} of the monocomponent fluid is related to the packing fraction ϕ of the polydisperse mixture through

$$\frac{\phi_{\text{eff}}}{1-\phi_{\text{eff}}} = \lambda^{-1}\frac{\phi}{1-\phi}. \qquad (2)$$

In order to fix the parameters α and λ, consistency of Eq. (1) to third order in density is imposed. This leads, in the three-dimensional case, to $\lambda = M_3 M_1/M_2^2$ and $\alpha = M_3 M_1^3/M_2^3$, with $M_n = \int_0^\infty d\sigma\, \sigma^n f(\sigma)$ being the nth moment of the size distribution $f(\sigma)$.

An interesting consequence of Eq. (1) is that one can invert it to *infer* the monocomponent EoS from that of the polydisperse fluid. The degree of collapse of the mapping from different functions $Z(\phi)$ onto a *common* function $Z_p(\phi_{\text{eff}})$ is an efficient way of assessing Eq. (1) without having to use an externally imposed EoS.

In this work we will assume heuristically that, in the case of hard disks (HD), the relationships between Z and Z_p and between ϕ and ϕ_{eff} have precisely the form of Eqs. (1) and (2). In this case we will also fix α and λ by imposing the consistency of Eq. (1) at least up to third order in density. This leads to

$$\lambda = \frac{\bar{B}_2 - 1}{b_2 - 1}\frac{b_3 - 2b_2 + 1}{\bar{B}_3 - 2\bar{B}_2 + 1}, \quad \alpha = \lambda^2\frac{\bar{B}_2 - 1}{b_2 - 1}, \qquad (3)$$

where $\bar{B}_n \equiv B_n/(\pi M_2/4)^{n-1}$ are reduced virial coefficients of the mixture (B_n being the standard coefficients) and $b_2 = 2$ and $b_3 = 4(4/3 - \sqrt{3}/\pi)$ are the (reduced) second and third virial coefficients of the monocomponent HD fluid, respectively. The second virial coefficient of the polydisperse HD mixture is given exactly by $\bar{B}_2 = 1 + M_1^2/M_2$. On the other hand, given a size distribution $f(\sigma)$, the *exact* third virial coefficient is also known, but unfortunately not expressible in terms of moments. Its explicit expression is

$$B_3 = \frac{\pi}{2}\int_0^\infty d\sigma_1\, f(\sigma_1)\int_0^\infty d\sigma_2\, f(\sigma_2)\sigma_{12}^2 \times \int_0^\infty d\sigma_3\, f(\sigma_3)\mathcal{A}_{\sigma_{13},\sigma_{23}}(\sigma_{12}), \qquad (4)$$

where $\sigma_{ij} = \frac{1}{2}(\sigma_i + \sigma_j)$ and $\mathcal{A}_{R_1,R_2}(r)$ is the intersection area of two circles of radii R_1 and R_2 whose centers are separated by a distance r [4].

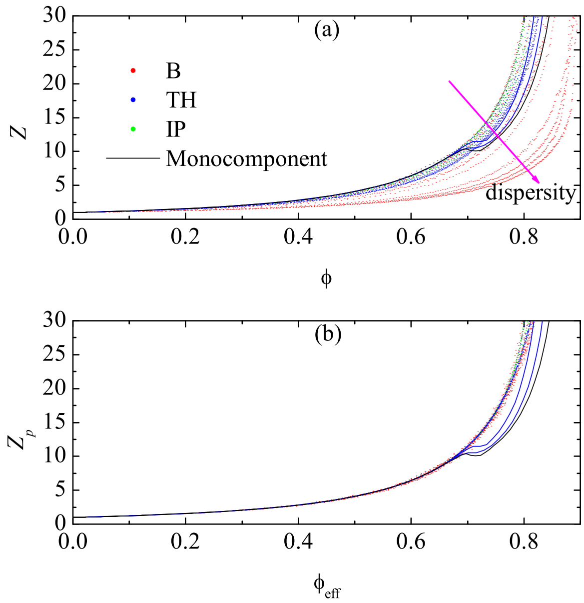

Figure 1: (a) Bare simulation values for different HD mixtures. (b) Inference of the EoS for the monocomponent fluid.

We have performed (event-driven) simulations to obtain data for the compressibility factor of the monocomponent fluid and of 26 polydisperse HD mixtures with different size distributions: binary (B), top-hat (TH), and inverse-power (IP). Those data have been used to assess the mapping "polydisperse HD mixture $\leftrightarrow$ monocomponent HD fluid" given by the ansatz (1). As observed in Fig. 1, the collapse of all the mixture curves is excellent in the stable region ($\phi_{\text{eff}} \lesssim 0.7$) and keeps being rather good (although, of course, not perfect) in the metastable region ($\phi_{\text{eff}} > 0.7$), except for two binary mixtures in which the ratio between the diameters of the biggest and the smallest disk is less than or equal to 1.2. Those latter curves exhibit crystallization effects in that region and thus follow trends similar to that of the monocomponent fluid. On the other hand, a higher degree of polydispersity allows one to frustrate equilibration to a crystal phase and explore the metastable fluid branch, which is practically inaccessible for the monocomponent fluid.

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