# A new Percus–Yevick equation of state for hard spheres, as derived from the chemical-potential route

Andrés Santos*
*Departamento de Física, Universidad de Extremadura, E-06071 Badajoz, Spain*

As is well known, the hard-sphere (HS) model is of great importance in liquid state theory from both academic and practical points of view. The model is also attractive because it provides a nice example of the existence of non-trivial exact solutions of an integral-equation theory, namely the Percus–Yevick (PY) theory.

As generally expected from an approximate theory, the radial distribution function (RDF) provided by the PY integral equation suffers from thermodynamic inconsistencies, i.e., the thermodynamic quantities derived from the same RDF via different routes are not necessarily mutually consistent. In particular, the PY solution for HSs of diameter $\sigma$ yields the following expression for the compressibility factor $Z \equiv p/\rho k_B T$ (where $p$ is the pressure, $\rho$ is the number density, $k_B$ is Boltzmann's constant, and $T$ is the temperature) through the virial (or pressure) route:

$$Z_v(\eta) = \frac{1+2\eta+3\eta^2}{(1-\eta)^2}. \tag{1}$$

Here, $\eta = \frac{\pi}{6}\rho\sigma^3$ is the packing fraction and the subscript $v$ is used to emphasize that the result corresponds to the virial route. In contrast, the compressibility route yields

$$Z_c(\eta) = \frac{1+\eta+\eta^2}{(1-\eta)^3}. \tag{2}$$

Equation (2) is also obtained from the scaled-particle theory (SPT). The celebrated and accurate Carnahan–Starling (CS) equation of state (EOS) is obtained as the simple interpolation

$$Z_{\text{CS}}(\eta) = \frac{1}{3}Z_v(\eta) + \frac{2}{3}Z_c(\eta) = \frac{1+\eta+\eta^2-\eta^3}{(1-\eta)^3}. \tag{3}$$

Except perhaps in the context of the SPT, little attention has been paid to the chemical-potential route to the EOS of HSs. In particular, the possibility of obtaining the EOS via this route by exploiting the exact solution of the PY equation for HS mixtures seems to have been overlooked. The aim of this work is to fill this gap and derive the result[1]

$$Z_\mu(\eta) = -9\frac{\ln(1-\eta)}{\eta} - 8\frac{1-\frac{31}{16}\eta}{(1-\eta)^2}, \tag{4}$$

where the subscript $\mu$ in Eq. (4) denotes that the compressibility factor is here obtained via the chemical-potential route. Equation (4) differs from Eqs. (1) and (2) in that it includes a logarithmic term and thus it is not purely algebraic. Nevertheless, $Z_\mu(\eta)$ is analytic at $\eta = 0$ and provides well-defined values for the (reduced) virial coefficients $b_n$ defined by $Z(\eta) = 1 + \sum_{n=2}^{\infty} b_n \eta^{n-1}$. Comparison of the first ten virial coefficients obtained from Eqs. (1), (2), and (4) with the exact analytical ($n = 2$–$4$) and Monte Carlo values shows that those given by the chemical-potential route are more accurate than those from the virial route, although less than the ones from the compressibility route. This suggests the possibility of exploring a CS-like interpolation of the form $Z_{\mu c}(\eta) = \alpha Z_\mu(\eta) + (1-\alpha)Z_c(\eta)$ with $\alpha > \frac{1}{3}$. A simple and convenient choice is $\alpha = \frac{2}{5}$. Thus,

$$\begin{aligned} Z_{\mu c}(\eta) &= \frac{2}{5}Z_\mu(\eta) + \frac{3}{5}Z_c(\eta) \\ &= -\frac{18}{5}\frac{\ln(1-\eta)}{\eta} - \frac{13-50\eta+28\eta^2}{5(1-\eta)^3}. \end{aligned} \tag{5}$$

The superiority of $Z_{\mu c}$ over $Z_{\text{CS}}$ is confirmed by Fig. 1, where the differences $Z_{\mu c} - Z_{\text{CS}}$ and $Z_{\text{MD}} - Z_{\text{CS}}$ (where $Z_{\text{MD}}$ denotes molecular dynamics simulation values[2]) are compared. As can be seen, $Z_{\mu c}$ is closer than $Z_{\text{CS}}$ to $Z_{\text{MD}}$ up to $\eta \simeq 0.46$.

Equation (4) can be further extended to additive mixtures with the result

$$\begin{aligned} Z_\mu &= \frac{1}{1-\eta} + 3\frac{M_1M_2}{M_3}\frac{\eta}{(1-\eta)^2} \\ &\quad -9\frac{M_2^3}{M_3^2}\left[\frac{\ln(1-\eta)}{\eta} + \frac{1-\frac{3}{2}\eta}{(1-\eta)^2}\right], \end{aligned} \tag{6}$$

where $M_n \equiv \sum_i x_i \sigma_i^n$.

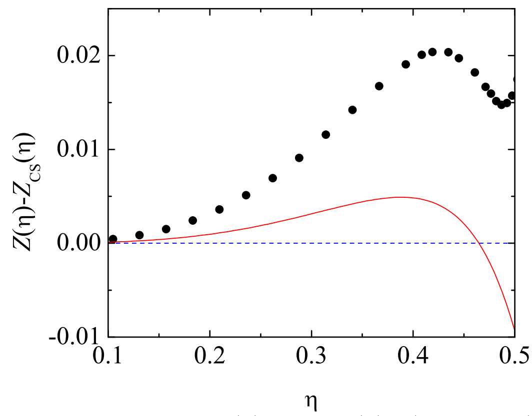


FIG. 1. Plot of $Z_{\mu c}(\eta) - Z_{\text{CS}}(\eta)$ (solid line) and $Z_{\text{MD}}(\eta) - Z_{\text{CS}}(\eta)$ (circles).

* andres@unex.es
`http://www.unex.es/eweb/fisteor/andres`

[1] A. Santos, unpublished (2012).

[2] S. Labík, J. Kolafa, and A. Malijevský, Phy. Rev. E **71**, 021105 (2005).