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A semi empirical compact equation of state for hard sphere fluids at any density

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ABSTRACT

We propose a new semi empirical expression of the equation of state for a hard sphere fluid which is valid in the disordered phases over the whole density range below and above the freezing point. Starting from the existing numerical results for the virial coefficients, we elaborate a compact expression for the equation of state which is compatible both with the low and medium density behaviour (disordered stable phase) and with the asymptotic high density behaviour (disordered metastable phase). The resulting equation of state has a compact form and exhibits a simple pole at the close random packing density and a double pole at a density equal to 1. That equation of state only depends on the following quantities: the virial coefficients B_2, B_3, B_4, which can be exactly computed, the random packing density ξ_0, which is imposed by statistical geometry, and the residue of the pole in ξ_0. The results are in a fairly good agreement with the numerical data.

1. Introduction

The random packing of a very high number of identical hard spheres in a large container is a useful model for simple fluids: rare gases at high density or liquid metals are examples of such fluids; it is also a model for colloids, granular and amorphous materials. Consequently, an enormous quantity of theoretical [1,2] as well as numerical [3–6] and experimental [7] works have been dedicated to the equation of state of hard sphere fluids.

An essential parameter is the packing factor ξ, which is the ratio of the actual volume of a system of spheres to the total volume they occupy. The pioneering experiments on model systems performed by Bernal et al. [8] and Scott et al. [9] have shown that the random packing density for hard spheres is very sensitive to experimental conditions. ξ can be increased up to a self-blocking situation ("loose random packing") whose precise value critically depends on the way the "fluid" has been poured into the container; by gently shaking or vibrating the container so as to simulate thermal agitation and to allow for local re-arrangements, the packing density comes closer to an upper limit ξ_0 ("close random packing") which is found to be about 0.637 [10,11] when one extrapolates the experimental points to an infinite sample i.e. when the boundary effects become negligible.

Molecular dynamics and Monte Carlo-type calculations have confirmed those results but actually extensive numerical simulations have evidenced a more complex behaviour [12]: in the absence of any attractive term in the molecular interaction, there is no thermally induced liquid – gas phase transition but freezing of the fluid phase can occur when the packing density exceeds a value $\xi_f \cong 0.495$. Above ξ_0 only the ordered phase exists, its density between ultimately capped by the fcc packing density $\xi_{fcc} = \pi 2^{1/2}/6 \cong 0.7405$. Between ξ_f and ξ_0 the fluid phase is metastable [13,14]: a randomly packed fluid is very sensitive to shearing, in contrast with a regularly packed medium, and the close random packing limit ξ_0 can be exceeded if some shearing, locally creating ordered domains, is applied; the actual system then presents a mixture of ordered and disordered areas, the so-called "jammed states" [15–17]. Melting of the ordered phase occurs when the density goes down backwards below $\xi_m \cong 0.545$.

Quite generally the fluid pressure can be expressed as an expansion in powers of the density, the "virial expansion". For a system of N identical hard spheres of diameter D in a container of volume V it can be written as

$$\frac{Pv}{k_B T} = \xi + 4\,\xi^2 + B_3\,\xi^3 + B_4\,\xi^4 + B_5\,\xi^5 + B_6\,\xi^6 + \dots \qquad (1)$$

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P is the pressure, $v = \pi D^3/6$ is the molecular volume, k_B is the Boltzmann constant, T is the absolute temperature and $\xi = Nv/V$ is the packing factor or reduced density. The number of particles N and the volume V are arbitrary large but finite, whereas ξ is a given finite parameter. In this expansion, the first term is the ideal gas term, the second one the mean-field term, the third term and the subsequent ones account for the molecular correlations; $B_3 = 10$, $B_4 = 18.364768\ldots$, the following coefficients can be computed numerically, the task getting increasingly harder with the order:

$$\frac{Pv}{k_BT} \cong \xi + 4\,\xi^2 + 10\,\xi^3 + 18.3648\,\xi^4 + 28.2245\,\xi^5 + 39.8151\,\xi^6 + 53.3444\,\xi^7 + \ldots \tag{2}$$

So far a large number of theoretical or semi-empirical equations of state, usually expressed as

$$\frac{PV}{Nk_BT} = f(\xi), \tag{3}$$

have been proposed for hard sphere systems [2]. In particular the famous Carnahan & Starling equation of state [18] is obtained by rounding the known virial coefficients as

$$\frac{PV}{Nk_BT} = 1 + 4\,\xi + 10\,\xi^2 + 18\,\xi^3 + 28\,\xi^4 + 40\,\xi^5 + 54\,\xi^6 \ldots\ . \tag{4a}$$

and extrapolating so that those coefficients appear to derive from a simple recursion

$$B_p = (p-1)(p+2) \tag{4b}$$

In compact form, the Carnahan & Starling equation of state is written as

$$\frac{PV}{Nk_BT} = \frac{1 + \xi + \xi^2 - \xi^3}{(1-\xi)^3} \tag{4c}$$

That expression is known to work remarkably well in the stable phase, i.e. for $\xi <\cong 0.5$, and even a little beyond in the metastable phase [19]. Now it is obvious that at high density it does not work any longer since it has a triple pole divergence for $\xi = 1$, whereas the equation of state should exhibit a simple pole for $\xi = \xi_0$; actually it is known from the asymptotic expression of the virial coefficients [20] that the equation of state at high density takes the following form [21,22]:

$$\frac{PV}{Nk_BT} \cong \frac{\lambda}{1 - \xi/\xi_0} \tag{5}$$

where λ is a numerical coefficient whose value is about 2.8; in the high density limit the virial coefficients are then given by

$$\lim_{p\to\infty} B_p = \frac{\lambda}{(\xi_0)^{p-1}} \tag{6}$$

In the present paper, starting from the existing numerical results for the virial coefficients, we intend to exhibit a compact expression for the equation of state which is simultaneously compatible both with the low and medium density behaviour (disordered stable phase) and with the asymptotic high density behaviour (disordered metastable phase). We will see that our resulting equation of state only depends on the following quantities: the virial coefficients B_2, B_3, B_4, which can be exactly computed, the random packing density ξ_0, which is imposed by statistical geometry, and the residue of the pole in ξ_0.

2. Derivation of the virial coefficients

In order to account for the pole in $\xi = \xi_0$ it is necessary for the equation of state to have the following form:

$$\frac{PV}{Nk_BT} = 1 + 4\xi + 10\xi^2 \frac{f_1(\xi)}{1 - \xi/\xi_0} \tag{7}$$

We develop $f_1(\xi)$ as a series of the density

$$\frac{PV}{Nk_BT} = 1 + 4\xi + 10\xi^2 \left(\frac{1 + a_4\xi + a_5\xi^2 + a_6\xi^3 + a_7\xi^4 + \ldots}{1 - \xi/\xi_0} \right). \tag{8}$$

By construction, that equation of state is consistent with the low density limit ($\xi \to 0$) and the high density limit ($\xi \to \xi_0$). In particular it is known that for hard spheres [1,2] the compressibility factor PV/Nk_BT and the contact value of the pair correlation function $g^{HS}(R = D_+)$ are connected through

$$\frac{PV}{Nk_BT} = 1 + 4\xi\, g^{HS}(R = D_+) \tag{9}$$

We see in the expression Equ. (8) that we recover the expected low density behaviour

$$\lim_{\xi\to 0} \frac{PV}{Nk_BT} = 1 + o(\xi) \text{ and } \lim_{\xi\to 0} g(R = D_+) = 1 + o(\xi).$$

By identification of Equ. (8) with the virial expansion we get

$$\begin{aligned} B_4/10 &= (\xi_0)^{-1} + a_4 \\ B_5/10 &= (\xi_0)^{-2} + (\xi_0)^{-1} a_4 + a_5 \\ B_6/10 &= (\xi_0)^{-3} + (\xi_0)^{-2} a_4 + (\xi_0)^{-1} a_5 + a_6 \\ &\ldots \end{aligned} \tag{10a}$$

or equivalently

$$\begin{aligned} B_5 &= (\xi_0)^{-1} B_4 + 10\, a_5 \\ B_6 &= (\xi_0)^{-1} B_5 + 10\, a_6 \\ B_7 &= (\xi_0)^{-1} B_6 + 10\, a_7 \\ &\ldots \end{aligned} \tag{10b}$$

i.e. for $p \geq 4$

$$a_p = \left(B_p - (\xi_0)^{-1} B_{p-1} \right) \big/ 10 \tag{11}$$

Fig. 1 shows the virial coefficients B_p derived from the numerical results by Clisby & Mc Coy for p = 1 to p = 10 [23] and from the results recently published by Wheatley for p = 11 and p = 12 [24]. If we consider those latter data, the curve $B_p(p)$ seems to exhibit an angular point for p = 11. Now it is known that both the pressure $P(\xi)$ and its derivative $\partial P(\xi)/\partial\xi$ which is proportional to the isothermal compressibility are continuous in the transition from the low and medium density regime to the asymptotic regime; we thus believe that the numerical value for B_{12} is doubtful. Nevertheless, the uncertainty attached to it is large ($\sigma \approx 26\%$); we have thus chosen to retain a corrected value at 1.3 σ so as to suppress the angular point.

Table 1 shows the a_p coefficients, the inverse values a_p^{-1} and the ratios a_{p+1}/a_p, for p = 4 to p = 12. The a_p^{-1} decrease regularly in absolute value and seem to go to 0 whereas the ratio a_{p+1}/a_p decreases to a constant value $\alpha \approx 1.30$. Consequently for p high enough the a_p behave like α^p, which suggests that $f_1(\xi)$ has a simple