Equation of state and the freezing point in the hard-sphere model

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The merits of different analytical equations of state for the hard-sphere system with respect to the recently computed high-accuracy value of the freezing-point packing fraction are assessed. It is found that the Carnahan–Starling–Kolafa and the branch-point approximant equations of state yield the best performance.

Despite the simplicity of the hard-sphere (HS) intermolecular potential and the vast amount of studies devoted to this model, up to date no one has been able to derive analytically neither the free energy nor the phase diagram of the HS system. Therefore, many of the important results concerning the equilibrium properties of the HS model have been obtained from computer simulations. It is well known that in the HS system the absolute temperature $T$ only enters as a scaling parameter and so its equilibrium phase diagram is usually presented as a graph in the pressure ($p$) vs density ($\rho$) or compressibility factor ($Z = \rho/k_B T$, with $k_B$ the Boltzmann constant) vs packing fraction ($\eta = \rho/\sigma^3$, $\sigma$ being the diameter of the spheres) planes. The characteristics of this phase diagram are relatively well understood, at least qualitatively. It comprises a stable fluid branch going from $\eta = 0$ to the freezing packing fraction $\eta_c \simeq 0.492$, where a fluid-solid phase transition takes place; a region of fluid-solid coexistence from $\eta_c$ to the crystal melting point packing fraction $\eta_m \simeq 0.543$; and finally a stable solid (crystalline) branch from $\eta_m$ to the close-packing fraction $\eta_{cp} = \frac{\sqrt{3}}{4} \simeq 0.7405$, corresponding to face-centered-cubic close-packing where $Z(\eta_{cp}) \to \infty$. Beyond the freezing point there is also a region of metastable fluid states that is supposed to end at the packing fraction $\eta_g \simeq 0.585$ where a widely accepted glass transition for the HS system occurs. The glass branch ends at the packing fraction $\eta_{gfp} \simeq 0.64$ corresponding to the random close-packing of an amorphous solid where also $Z(\eta_{gfp}) \to \infty$. There is further a region of metastable crystalline states for packing fractions below $\eta_g$.

Recently, accurate tethered Monte Carlo (MC) simulations have been reported in which the fluid-solid coexistence pressure ($p_{coex}$) of the HS system was computed, namely $p_{coex} = 11.5727(10) k_B T/\sigma^3$, the number enclosed by parentheses denoting the statistical error. The specific volumes associated with the freezing and melting points were also reported with the values $v_f = 1/\rho_f = 1.06448(10) \sigma^3$ and $v_m = 1/\rho_m = 0.96405(3) \sigma^3$, respectively.

Given these results, the aim of this Note is to explore whether starting with the above high-accuracy estimate of $p_{coex}$ and determining the freezing-point packing fraction (with its associated statistical error) from available analytical equations of state (EOS) one may conclude which equation of state yields the best performance near the freezing point. To this end we will examine the following (considered to be very accurate) four analytical EOS. First, we recall the celebrated Carnahan–Starling–Kolafa (CSK) EOS:

$$Z_{CS} = \frac{1 + \eta + \eta^2 - \eta^3}{(1 - \eta)^3}. \quad (1)$$

Next, we consider Kolafa’s correction, i.e., the Carnahan–Starling–Kolafa (CSK) EOS:

$$Z_{CSK} = \frac{1 + \eta + \eta^2 - \frac{2}{3}(1 + \eta)\eta^3}{(1 - \eta)^3}. \quad (2)$$

As a third EOS, a proposal based on the so-called rescaled virial (RV) expansion will also be included, namely

$$Z_{RV} = \frac{1 + \sum_{n=1}^{6} C_n \eta^n}{(1 - \eta)^3}, \quad (3)$$

with $C_1 = C_2 = 1$, $C_3 = -(19 - 4b_1)$, and $C_n = \sum_{j=0}^{3} \binom{3}{j} (-1)^{j+1} b_{n-2+j}$ for $n = 4-6$, $b_j$ being the (reduced) virial coefficients. Finally, a recently proposed branch-point (BP) approximant will be considered. It reads

$$Z_{BP} = 1 + \frac{1 + \sum_{n=1}^{3} \eta^n - (1 + 2a_1 \eta + a_2 \eta^2)^{3/2}}{4(1 - \eta)^3}, \quad (4)$$

with $a_1 = -C_5/C_4$, $a_2 = 7a_1^2 - 6C_6/C_4$, $A = -\frac{3}{8}(a_2 - a_1^2)^2/C_4$, $c_1 = 3a_1 + 4A$, $c_2 = \frac{3}{2}(a_2 + a_1^2) - 2A$, and $c_3 = \frac{3}{8}a_1(3a_2 - a_1^2) + (b_4 - 18)A$.

Since the procedure involves inverting Eqs. (1)–(4) to compute $\eta_f$ (and its statistical error $\Delta \eta_f$) from the MC value of $p_{coex}$ (and its associated statistical error $\Delta p_{coex}$), this may in general only be achieved numerically. A simple approach to determine both $\eta_f$ and $\Delta \eta_f$ is to employ a MC method involving the following steps:

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from the value of the freezing-point specific volume $v$ and whose standard deviation is equal to the statistical error $(\sigma^3/k_BT)\Delta p_{\text{coex}}$ coming out of the simulations.

2. A value of the packing fraction $\eta$ is derived using Newton’s method through the equation $\frac{d}{d\eta}Z(\eta) = p$, where $Z(\eta)$ is the compressibility factor corresponding to each one of the above EOS.

3. Step 1 is repeated so as to gather a statistically representative set of $N$ values of $\eta$.

4. Finally $\eta$ is taken as the average of the above solutions and the standard deviation $\Delta \eta$ is equated to the associated statistical error.

After applying the previous procedure to each one of the EOS (1)-(4) and taking in every case the statistics over $N = 5 \times 10^6$ elements, the results shown in Table I were obtained. The simulation value of $\eta$ that follows from the value of the freezing-point specific volume $v_f$ stated earlier is also included in Table I.

One should add in connection with Eqs. (3) and (4) that the virial coefficients used in them are not all exactly known. In fact, only the second, third, and fourth virial coefficients are exact and given by known. In fact, only the second, third, and fourth virial coefficients are exact and given by

$$b_2 = 28.22445(10), \quad b_3 = 39.81550(36), \quad b_4 = 53.3413(16).$$

We have also accounted for the statistical errors associated with $b_5-b_7$ and recalculated the corresponding error bars of $\eta$ by means of the MC procedure described above, this time with $N = 1.5 \times 10^6$. The outcome has been $\eta = 0.491820(10)$ and $\eta = 0.491917(10)$ for the RV and BP EOS, respectively. Therefore, the influence of the statistical errors of the virial coefficients on the RV and BP values is practically negligible.

The results of Table I are graphically displayed in Fig. 1. It is clear that the best performance with respect to the simulation results is provided by both $Z_{\text{CSK}}$ and $Z_{\text{BP}}$, with possibly a slight superiority of the latter. Whereas $Z_{\text{CSK}}$ is simpler than $Z_{\text{BP}}$, the latter has the advantage of predicting a physical value (smaller than $\eta_{\text{coex}}$) for the radius of convergence of the virial series. 1,13

| Method | $\eta$       |
|--------|-------------|
| MC     | 0.491882(46)|
| CS     | 0.491972(10)|
| CSK    | 0.491297(10)|
| RV     | 0.491816(10)|
| BP     | 0.491913(10)|

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