

Comment on “A Highly Accurate and Analytic Equation of State for a Hard Sphere Fluid in Random Porous Media”

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In a recent paper,¹ two of us (M.H. and W.D.) developed a scheme based on the scaled particle theory (SPT) to derive analytical equations of state (EOS) for a hard sphere fluid in random porous media. Despite the fine agreement between the SPT and simulation results² (errors $\leq 20\%$), we will show here that an inconsistency exists in that SPT formulation and present its correction. Although the results given in eqs 29–31 in the paper of H. Holovko and W. Dong¹ allow for calculating readily the pressure of a hard sphere (HS) fluid in a hard sphere matrix, no result for pressure was presented. From eq 29 in ref 1, one obtains immediately

$$\frac{\beta P}{\rho_1} = \frac{1}{\eta_1} \left\{ \beta \mu_1^{\text{ex}} + \ln(1 - \eta_0 - \eta_1) - \frac{3[\eta_0\tau(\tau + 1) + 2\eta_1]}{1 - \eta_0 - \eta_1} - \frac{9(\eta_0\tau + \eta_1)^2}{2(1 - \eta_0 - \eta_1)^2} \right\} \quad (1)$$

where all of the notations are identical to those used in ref 1.

In the limit of $\rho_1 \rightarrow 0$, the fluid becomes an ideal gas in a HS matrix, and its EOS is simply

$$\beta P = \rho_1 \quad (2)$$

We will show now that eq 1 does not yield this EOS when $\rho_1 \rightarrow 0$. For $\rho_1 \rightarrow 0$, eq 30 in ref 1 becomes

$$\beta \mu_1^{\text{ex}} = \beta \lim_{\rho_1 \rightarrow 0} W_0(R_1) = -\ln(1 - \eta_0) + \frac{3\eta_0\tau}{1 - \eta_0} + \frac{3\eta_0(2 + \eta_0)\tau^2}{2(1 - \eta_0)^2} + \frac{\eta_1\beta P_0}{\rho_1} \quad (3)$$

where

$$\beta P_0 = \rho_0(1 + \eta_0 + \eta_0^2)/(1 - \eta_0)^3 \quad (4)$$

and eq 31 in ref 1 is used to obtain the result on the right-hand side (RHS) of eq 3. The first three terms on the RHS of eq 3 cancel exactly the last three terms on the RHS of eq 1, and substituting eq 3 into eq 1 leads to

$$P = P_0 \quad (5)$$

where P_0 is given by eq 4. When the matrix is present, that is, $\rho_0 \neq 0$, $P_0 \neq 0$, and the result in eq 5 is clearly in contradiction with the exact result for an ideal gas in a HS matrix given in eq 2. In the case of an overlapping HS matrix, we obtain the same result as that in eq 5 but with $\beta P_0 = \rho_0$ instead of eq 4.

We can also see the inconsistency in an alternative way. In the paper of M. Holovko and W. Dong, the result given in eq 30 is obtained by taking the derivative of eq 29 with respect to η_1 , then eliminating $(\partial P/\partial \eta_1)_{T,\rho_0}$ with the help of the Gibbs–Duhem equation, and integrating finally the first-order differential equation for the chemical potential. In fact, we can also calculate the chemical potential alternatively as follows. Instead of eliminating $(\partial P/\partial \eta_1)_{T,\rho_0}$, we can eliminate $(\partial \mu/\partial \eta_1)_{T,\rho_0}$ and obtain a first-order differential equation for P instead for μ_1 . Integrating this equation from the fluid packing fraction equal to zero to η_1 and using $P(\eta_1 = 0) = 0$ (see eq 2) for determining the integration constant, we obtain an expression for P , and substituting this result into eq 29 of ref 1 yields an expression for the chemical potential. However, this result for the chemical potential is not equal to that given in the eq 30 of ref 1 but different by a term equal to $4\pi R_1^3 P_0/3$ with P_0 given by eq 4.

From the above investigations, it turns out that the extrapolation formula given in eq 8 of ref 1 is not totally appropriate for confined fluids and that it should be modified to

$$W(R_s) = \frac{4\pi R_1^3}{3} (P + w_3^0)(1 + R_s/R_1)^3 + 4\pi R_1^2 \gamma(R_s)(1 + R_s/R_1)^2 \quad (6)$$

Now, we explain the reason to introduce the term, w_3^0 , and its meaning. For a bulk fluid, inserting a single particle into an empty system (i.e., without any other fluid particle) does not require any work. In contrast, inserting a single fluid particle into an empty matrix requires some work since a pore with a size equal to at least that of the fluid particle must be found. For a single HS in a HS matrix, the result of SPT for this work, $W_0(R_1)$, is given in eq 31 of ref 1. $W_0(R_1)$ contains a term proportional to $4\pi R_1^3/3$, and we denote its coefficient as w_3^0 . Although w_3^0 has the unit of pressure (equal to P_0 in the cases of a single HS in a HS or an overlapping HS matrix), it is not a contribution to the fluid pressure, and its contribution should not be counted into the fluid pressure. Therefore, the modified extrapolation formula given in eq 6 allows for obtaining the consistent result for the fluid pressure.

It is to be pointed out that although eq 8 in ref 1 contains the inconsistency described above, the results for chemical potential obtained by integrating $(\partial \mu/\partial \eta_1)_{T,\rho_0}$ as done in ref 1 are correct. Now, by using eq 6, correct results can be obtained by integrating either $(\partial \mu/\partial \eta_1)_{T,\rho_0}$ or $(\partial P/\partial \eta_1)_{T,\rho_0}$.

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References and Notes

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