

Nonmonotonous pressure as a function of the density in a fluid without attractive forces

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A simple result for the pressure of a hard sphere fluid that was developed many years ago by Rennert is extended in a straightforward manner by adding the terms that are of the same form as the Rennert's formula. The resulting expression is moderately accurate but its accuracy does not necessarily improve as additional terms are included. This expression has the interesting consequence that the pressure can have a maximum, as the density increases, which is consistent with the freezing of hard spheres. This occurs solely as a consequence of repulsive interactions. Only the Born-Green-Yvon and Kirkwood theories show such a behavior for hard spheres and they require a numerical solution of an integral equation. The procedure outlined here is *ad hoc* but is, perhaps, useful just as the popular Carnahan-Starling equation for the hard sphere pressure is also *ad hoc* but useful.

Key words: partition function, equation of state, pressure, hard sphere fluid, freezing transition

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1. Introduction

For a number of years, the author has been intrigued by a result obtained by Rennert [1] for a hard sphere fluid. For this fluid, the interaction potential, $u(R_{12})$, for a pair of spheres whose centers are located at \mathbf{r}_1 and \mathbf{r}_2 , vanishes if the separation of the centers, $R_{12} = |\mathbf{r}_1 - \mathbf{r}_2|$, exceeds their diameter, d . Since the spheres are hard, they cannot overlap and $u(R)$ is infinite if $R < d$. To keep the discussion simple, here the hard spheres are all assumed to be of the same diameter. Hard spheres are important because the 'structure' of a simple liquid or dense gas, such as argon, is, apart from the small perturbing effect of the attractive dispersion forces, determined by hard sphere interactions [2].

The connection between the pressure of a fluid of N molecules and their interactions is provided by the configurational partition function, Q_N ,

$$Q_N = \frac{1}{N!} \int \exp[-\beta U(\mathbf{r}_1, \dots, \mathbf{r}_N)] d\mathbf{r}_1, \dots, d\mathbf{r}_N, \quad (1)$$

where $\beta = 1/kT$, and k and T are the Boltzmann constant and temperature, respectively. The interaction energy U is assumed to be the pairwise additive sum of the pair potentials,

$$U(\mathbf{r}_1, \dots, \mathbf{r}_N) = \sum_{i < j = 1}^N u(r_{ij}). \quad (2)$$

The challenge is to determine the configurational partition function, since once it is known, the density dependent part of the Helmholtz function, A , and the pressure, p , for a given value of the density, $\rho = N/V$, where V is the volume, can be obtained from

$$A = -kT \ln Q_N \quad (3)$$

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and

$$p = -\frac{\partial A}{\partial V}. \quad (4)$$

Since N is enormous (of the order of Avogadro's number), this can be done only approximately.

2. Rennert's method

Rennert considers a collection of systems that have n hard spheres, where n is a variable. He defines

$$q_n = \frac{Q_{N+1}}{VQ_N}, \quad (5)$$

$Q(0) = 1$. From this it follows that

$$\frac{p}{\rho kT} = 1 - \rho \frac{\partial}{\partial \rho} \left[\frac{1}{N} \int_0^N \ln q_n dn \right]. \quad (6)$$

Reasoning by analogy to one dimension, Rennert suggests the ansatz

$$\ln q_n = \left(1 - \frac{nv_d}{V}\right) - \epsilon \frac{nv_d}{V - nv_d} \quad (7)$$

from which, after some algebra, it follows that

$$\frac{p}{\rho kT} = \frac{\epsilon}{1 - \rho v_d} - \frac{1 - \epsilon}{\rho v_d} \ln(1 - \rho v_d), \quad (8)$$

where v_d and ϵ are the parameters to be chosen. In one dimension, Rennert chooses $v_d = d = b$, where $B_2 = b$ is the correct second virial coefficient in one dimension, and $\epsilon = 0$. The choice $v_d = d$ is sensible because for $\rho d = 1$, the hard particles fill space and a singularity is to be expected. The virial coefficients for one dimensional hard particles that result from equation (8) are

$$B_n = \frac{1 + (n-1)\epsilon}{n} d^{n-1}. \quad (9)$$

They are correct with $\epsilon = 0$. The resulting equation of state is

$$\frac{p}{\rho kT} = \frac{1}{1 - y}, \quad (10)$$

which, for hard particles in one dimension, is exact.

Rennert also applied equation (8) in three dimensions (hard spheres). With the choices, $v_d = B_2 = b = 2\pi d^3/3$ and $\epsilon = 8\pi/3\sqrt{2} - 1$, equation (8) yields the correct second and third virial coefficients for hard spheres. As is seen in figure 1, Rennert's procedure gives fair results for hard spheres. In summary, for hard particles, using equation (8) and choosing v_b so that ρ_b is the density at close packing and ϵ yields the correct second virial coefficient, exact results are obtained in one dimension and fair results are obtained in three dimensions.

3. Extension

A reasonable extension of equation (7) is

$$\ln q_n = \ln \left(1 - \frac{nv_d}{V}\right) - \sum_{i=1}^{\infty} \epsilon_i \left(\frac{nv_d}{V - nv_d}\right)^i, \quad (11)$$

which, neglecting the terms in the sum for $i > 4$ leads to the following extension of equation (8)

$$\frac{p}{\rho kT} = -\frac{1}{\rho v_d} \ln(1 - \rho v_d) + \sum_{i=1}^4 a_i \epsilon_i, \quad (12)$$

where

$$a_1 = \frac{1}{\rho v_d} \ln(1 - \rho v_d) + \frac{1}{1 - \rho v_d}, \quad (13)$$

$$a_2 = -\frac{2}{\rho v_d} \ln(1 - \rho v_d) - 3 \frac{1}{1 - \rho v_d} + \frac{1}{(1 - \rho v_d)^2}, \quad (14)$$

$$a_3 = \frac{3}{\rho v_d} \ln(1 - \rho v_d) + \frac{11}{2(1 - \rho v_d)} - \frac{7}{2(1 - \rho v_d)^2} + \frac{1}{(1 - \rho v_d)^3}, \quad (15)$$

and

$$a_4 = -\frac{4}{\rho v_d} \ln(1 - \rho v_d) - \frac{25}{3(1 - \rho v_d)} + \frac{23}{3(1 - \rho v_d)^2} - \frac{13}{3(1 - \rho v_d)^3} + \frac{1}{(1 - \rho v_d)^4}. \quad (16)$$

Keeping only ϵ_1 yields Rennert's result. Each of the ϵ_i can be chosen to give B_{i+1} , which are known to high order [2]. The result for B_i that follows from the above result has a pleasing form. It is

$$B_i / v_b^{i-1} = \frac{1}{i} + \epsilon_1 \frac{i-1}{i} + \epsilon_2 \frac{(i-1)(i-2)}{i} + \epsilon_3 \frac{(i-1)(i-2)(i-3)}{2i} + \epsilon_4 \frac{(i-1)(i-2)(i-3)(i-4)}{6i} + \dots \quad (17)$$

The sum is terminated when a negative term is encountered. If one wishes to add an additional term in equation (12), the previously determined values of ϵ_i remain unchanged. In one dimension, $\epsilon_1 = 1$ and the additional $\epsilon_i = 0$. In three dimensions, $\epsilon_1 = 4.92384391$, $\epsilon_2 = 2.80081908$, $\epsilon_3 = -0.918729979$ and $\epsilon_4 = -0.218154034$.

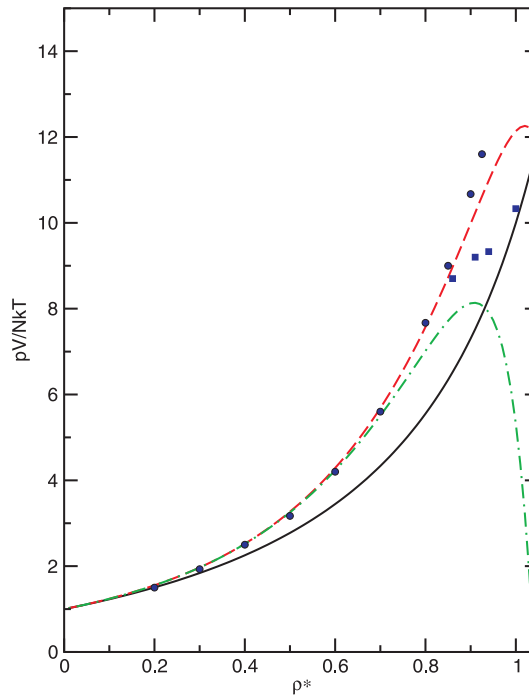


Figure 1. (Color online) Pressure of hard spheres as a function of density. The points give the simulation results taken from reference 2; the circles and squares give the simulation results for the fluid and solid branches, respectively. The solid curve gives the results obtained from equation (8). The dashed and dot-dashed curves give the results obtained from equation (12) with ϵ_i included for $i \leq 3$ and $i \leq 4$, respectively.

Results for $p/\rho kT$ as a function of ρ for hard spheres (three dimensions) are given in figure 1 when the series is terminated after ϵ_1 , ϵ_3 , and ϵ_4 . The results for the case where only ϵ_1 is included because this is Rennert expression. In this case, the pressure is monotonous. Results for the cases when the series terminates after ϵ_2 are not included because the pressure is monotonous. The displayed curves are

compared with the results of computer simulations taken from [2]. The simulation curves consist of two branches, one for the fluid branch and one for the solid branch, which terminates at close packing. The agreement is quite reasonable. However, the most intriguing feature is not the numerical accuracy of this procedure that, for the fluid branch, is not quite as good as that of the *ad hoc* Carnahan-Starling [3] expression but the fact that with terms through ϵ_3 or ϵ_4 included in equation (12), there is a maximum in the pressure at approximately the location of the transition from the fluid to the solid phases. Better results are given with ϵ_4 included but neglecting the contribution of ϵ_4 does a better job of locating the transition. It is reasonable to regard this maximum as indicative of the freezing of the hard sphere fluid, since a system with a negative compressibility would expand with an increase of pressure, which is unphysical. The Carnahan-Starling expression does not give any indication of the presence of this transition and, in fact, is unphysical at very high densities since it continues to give results for densities past close packing. To be sure, the procedure reported here is *ad hoc*. There is no guarantee that including more ϵ_i will continue to give better results or even a maximum pressure. In fact, this is the situation in two dimensions where neglecting ϵ_4 yields a maximum while including ϵ_4 does not. The point of this article is to point out that this procedure does give an indication of a phase transition in a hard sphere fluid. To the author's knowledge, beyond the more complex Born-Green-Yvon [4–6] and Kirkwood [7] approximations, this is the only theory to do so. This paper might probably point the way to a simple non-empirical description of the hard sphere transition and be useful in this regard.

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References

1. Rennert P., Z. Naturforsch, 1967, **22**, 981.
2. Barker J.A., Henderson D., Rev. Mod. Phys., 1976, **48**, 587; doi:10.1103/RevModPhys.48.587.
3. Carnahan N.F., Starling K.E., J. Chem. Phys., 1969, **51**, 635; doi:10.1063/1.1672048.
4. Born M., Green H.S., P. R. Soc. London A-Conta., 1946, **188**, 10; doi:10.1098/rspa.1946.0093
5. Born M., Green H.S., P. R. Soc. London A-Conta., 1947, **191**, 168; doi:10.1098/rspa.1947.0108.
6. Yvon J., Actualités Scientifiques et Industrielles, 1935, **203**.
7. Kirkwood J.G., Maun E.K., Alder B.J., J. Chem. Phys., 1950, **18**, 1040; doi:10.1063/1.1747854.

Немонотонний тиск як функція густини у плинні без притягальних сил

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Простий результат для тиску плинну твердих сфер, який був отриманий багато років тому Реннертом, розширено в простий спосіб шляхом додавання членів, які мають такий же вигляд як формула Реннерта. Результируючий вираз є посередньо точним, але його точність не обов'язково покращиться, якщо включити додаткові члени. Цікавим наслідком отриманого виразу є те, що тиск може мати максимум, коли густина зростає, що узгоджується із твердженням твердих сфер. Це відбувається виключно як наслідок короткодійних взаємодій. Лише теорії Борна-Гріна-Івона і Кірквуда показують таку поведінку для твердих сфер і вони потребують числового розв'язку інтегрального рівняння. Процедура, окреслена тут є *ad hoc*, але можливо є корисною такою ж мірою, як і популярне рівняння Карнагана-Старлінга для тиску твердих сфер, яке є також *ad hoc*, але корисним.

Ключові слова: статистична сума, рівняння стану, тиск, плин твердих сфер, перехід тверднення