

Equilibrium Theory for the Hard-Core Systems

Shigeru Shinomoto¹

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It is found that the density expansion in the argument of the exponential function gives a fine convergence on the equation of state of the hard-sphere system. The pair distribution function and the equation of state is constructed by an intuitive kinetic theoretical method. The equation of state of the hard-core system with attractive potential is constructed semiempirically with the aid of this simple analytical result, and Kamerling-Onnes' constant of the critical point is obtained analytically.

KEY WORDS: Equation of state; pair distribution function; cluster expansion; kinetic theory; hard-sphere system; critical point.

1. INTRODUCTION

Since Kirkwood and Mayer presented the methodologies of obtaining the pair distribution function and the equation of state, fine approximate equations such as Yvon-Born-Green (YBG) equation, Percus-Yevick (PY) equation and the hypernetted-chains (HNC) equation were obtained. In spite of this, there are still many remaining problems. In particular, there was no guiding principle on what we should choose for the dense fluid as an expansion parameter. Thus, though more diagrams are retained in the HNC equation than in the PY equation, it seems that the PY equation gives better numerical results than the HNC equation.

In this paper, we show that the equation of state of the hard-sphere system may be approximated well by the density expansions in the argument of the exponential function. This calculation is easily performed up to the second order in density by an elementary kinetic theoretical method. The resulting equation of state has a simple analytical form and exhibits a

¹ Department of Physics, Faculty of Science, Tohoku University, Sendai, 980, Japan.

quite fine agreement with experimental results in the whole region of the fluid phase.

By means of this equation of state, we shall construct a semiempirical one for the hard-core system with attractive potential. This also gives a quite simple analytical solution of the density for the critical point.

2. THE HARD-SPHERE SYSTEM

2.1. Pair Distribution Function

We show a method to obtain the pair distribution function from an intuitive consideration preliminarily given in the previous article.⁽¹⁾ The pair distribution is enhanced near the contact distance σ which is a diameter of the particle. This has been interpreted intuitively.⁽²⁾ Let a particle be fixed at the origin, and a second particle be fixed at a distance r ($\sigma < r < 2\sigma$) from the first. The centers of the other particles can not enter the overlapping "spheres of influence" or "covering spheres" defined as concentric spheres of radius σ of the two fixed particles. As a result, the second particle suffers less collisions on the side facing the first than on the opposite side. This induces a mean attractive force on the second toward the first (see Fig. 1).

It is interesting to construct the pair distribution function directly from this consideration.

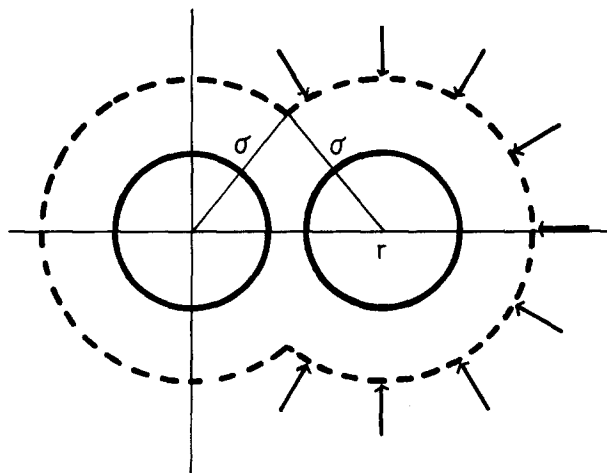


Fig. 1. A situation that a particle is at the origin and a second particle is at a distance r ($\sigma < r < 2\sigma$) from the first. The dashed circles represent the "sphere of influence."

First, we assume that the effect of the other particles can be treated as a mean “pressure” \tilde{P} on the sphere of influence. Then, the mean “force” can be expressed as

$$\mathbb{F}_p(r) = \int_R d^2\Omega \tilde{P} \quad (2.1)$$

where $d^2\Omega$ denotes the surface element and R is the part of the surface that does not overlap. Furthermore, if we assume the uniformity of this pressure, it is easily found

$$F_p(r) = -\tilde{p}\pi\sigma^2 [1 - (r/2\sigma)^2] \quad (2.2)$$

for $\sigma < r < 2\sigma$.

As the second particle is brought adiabatically from infinite distance to distance r , the work or the potential of mean “force” becomes

$$\Phi_p(r) = -\int_{2\sigma}^r dr' F_p(r') = -\frac{\pi}{6} \sigma^3 \tilde{p} \phi(r) \quad (2.3)$$

for $\sigma < r < 2\sigma$, where $\phi(r)$ is defined as

$$\phi(r) = \frac{1}{2} \left(\frac{r}{\sigma} - 2 \right)^2 \left(\frac{r}{\sigma} + 4 \right) \quad (2.4)$$

The probability of finding a particle on condition that another particle is at the origin may be put equal to the Boltzmann factor:

$$g(r) = \exp[-\Phi_p(r)/kT] \quad (2.5)$$

where k is the Boltzmann constant and T is the temperature.

The mean pressure \tilde{p} is obtained from the elementary kinetic theory as

$$\tilde{p} = \tilde{n}kT \quad (2.6)$$

where \tilde{n} is the density at the surface of the overlapping spheres of influence. For moderately dense gases, we may expect that many particles seldom gather together and approximate this density by the average density of the whole system, n .

Then, the pair distribution function becomes

$$g(r) = \exp[y\phi(r)] \quad (2.7)$$

where

$$y \equiv (\pi/6)\sigma^3 n \quad (2.8)$$

is the ratio of the total volume occupied by the spheres to the volume of the system.

This result turns out to be the “first” approximation of the YBG equation and at the same time the potential of mean “force” here is

identified as the leading term in the density expansion of $\Phi_p(r)$:

$$g(r) = e^{n \circlearrowleft} = 1 + n \circlearrowleft + \frac{n^2}{2!} \circlearrowleft + \frac{n^3}{3!} \circlearrowleft + \dots \quad (2.9)$$

Here, the graph is defined as

$$\circlearrowleft \equiv \int d^3r_3 f_{13} f_{23} \quad (2.10)$$

where f_{ij} is the Mayer function.

The way to obtain more elaborate treatments is to improve the uniformity assumption of the mean “pressure,” which can readily reproduce the YBG equation that is found in the usual configuration integration method.⁽²⁾

2.2. Equation of State

In the same way as the preceding subsection, we can calculate the density near the wall. When we fix a particle at a distance x ($\sigma/2 < x < 3\sigma/2$) from the wall, the centers of other particles cannot enter the overlapping “sphere of influence” and “plane of influence,” the latter being defined as the plane at the distance $\sigma/2$ from the wall. As a result, the

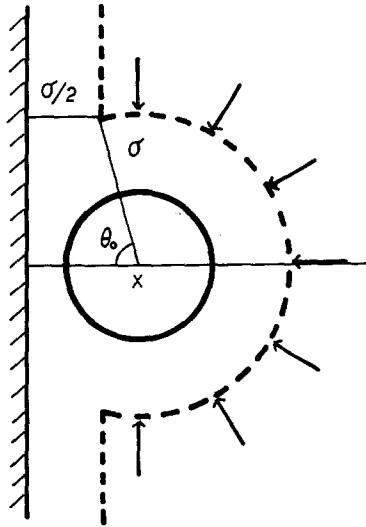


Fig. 2. A situation that a particle is at the distance x from the wall. The dashed line at the distance $\sigma/2$ from the wall represents the “plane of influence.”

particle suffers fewer collisions on the side facing the wall than on the opposite side. This induces a mean attractive force toward the wall (see Fig. 2). In other words, the particle is pressed onto the wall by other particles.

A calculation analogous to the one leading to Eq. (2.2) gives the mean "force":

$$F_s(x) = -\tilde{p}\pi\sigma^2\left(1 - \left(\frac{x}{\sigma} - \frac{1}{2}\right)^2\right) \quad (2.11)$$

for $\sigma/2 < x < 3\sigma/2$, and the potential of mean "force":

$$\Phi_s(x) = -\int_{3\sigma/2}^x dx' F_s(x') = -\frac{\pi}{6}\sigma^3\tilde{p}\psi(x) \quad (2.12)$$

$$\psi(x) \equiv 2\left(\frac{x}{\sigma} - \frac{3}{2}\right)^2\left(\frac{x}{\sigma} + \frac{3}{2}\right) \quad (2.13)$$

Then, the density near the wall becomes

$$n_s^{(1)}(x) = n \exp[\gamma\psi(x)] \quad (2.14)$$

where we have assumed that $\tilde{p} = nkT$. The density at the distance in contact with the wall becomes

$$n_{2s}^{(1)}(\sigma_+/2) = ne^{4\gamma} \quad (2.15)$$

where σ_+ means $\sigma + 0$.

Thus, we obtain the pressure on the wall:

$$P = n_s^{(1)}(\sigma_+/2)kT \quad (2.16)$$

and the equation of state:

$$P/nkT = \exp(4\gamma) \quad (2.17)$$

This equation of state has an analytical form completely different from the existing ones; they are algebraic functions of γ , while ours is a transcendental function. This is a first-order calculation in the argument of exponential function and we can proceed to the second approximation.

The only assumption we adopted in the argument above is the uniformity of the density, which breaks down in the denser system. There are mainly two causes that break the uniformity around the fixed particle near the wall. We already showed as the first approximation that there is a density gradient around the particle and near the wall. We should incorporate these when we proceed to the second approximation.

The inhomogeneity of the density causes the inhomogeneity of the "pressure." Then, the calculation of the mean "force" near the wall should

be written as

$$F_s^{(2)}(x) = \sigma^2 \int_{\theta_0}^{\pi} d\theta \int_0^{2\pi} d\phi \tilde{p}(x, \cos \theta) \cos \theta \sin \theta \quad (2.18)$$

where

$$\cos \theta_0 = \begin{cases} x/\sigma - 1/2 & \text{for } \sigma/2 < x \leq 3\sigma/2 \\ 1 & \text{for } 3\sigma/2 \leq x \end{cases}$$

and the “pressure” \tilde{p} is

$$\tilde{p}(x, \cos \theta) = \tilde{n}_s(x - \sigma \cos \theta) kT \quad (2.19)$$

The density \tilde{n}_s to be inserted is

$$\tilde{n}_s(x') = n_s^{(1)}(x') g(\sigma_+) \quad (2.20)$$

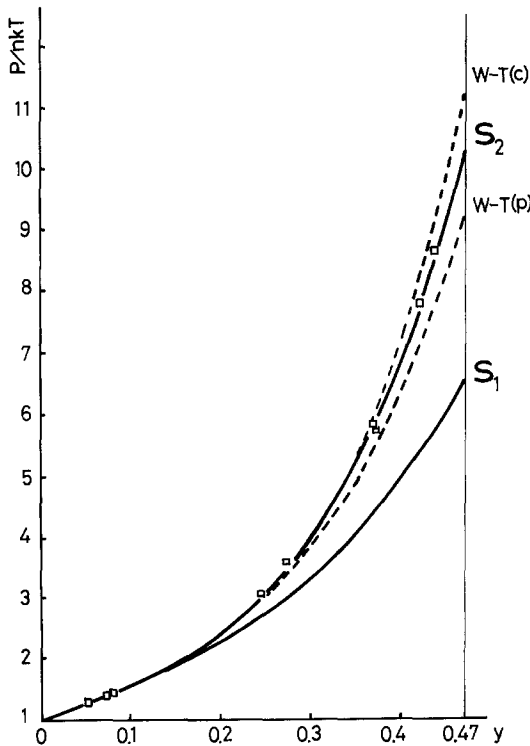


Fig. 3. Comparison of the equations of state to the molecular-dynamics results by Alder and Wainwright. S_1 is Eq. (2.17) and S_2 is Eq. (2.23). $WT(p)$ and $WT(c)$ are the Wertheim–Thiele solutions of PY equation (see Table I). The squares show the results obtained by Alder and Wainwright. $y = 0.47$ is the Alder transition density.

Table I. Virial Expansions^a

Exact		$1 + 4y + 10y^2 + 18.36y^3 + 28.2y^4 + 39.5y^5 +$
WT(p)	$\frac{1 + 2y + 3y^2}{(1 - y)^2}$	$1 + 4y + 10y^2 + 16y^3 + 22y^4 + 28y^5 +$
WT(c)	$\frac{1 + y + y^2}{(1 - y)^3}$	$1 + 4y + 10y^2 + 19y^3 + 31y^4 + 46y^5 +$
S_1	$\exp(4y)$	$1 + 4y + 8y^2 + 10.67y^3 + 10.67y^4 + 8.57y^5 +$
S_2	$\exp(4y + 2y^2)$	$1 + 4y + 10y^2 + 18.67y^3 + 28.67y^4 + 37.87y^5 +$

^aExact: Ree-Hoover result⁽⁴⁾; WT: Wertheim-Thiele solutions of PY equation; (p): the solution obtained by the pressure equation; (c): the solution obtained by the compressibility equation; S_1 : Eq. (2.17); S_2 : Eq. (2.23).

which corresponds to the superposition approximation. The potential of the mean "force" can be obtained as

$$\Phi_s^{(2)}(x) = - \int_{5\sigma/2}^x dx' F_s^{(2)}(x') \quad (2.21)$$

We carried out this calculation up to the second order in the density. This potential at the distance of the contact to the wall becomes

$$\Phi_s^{(2)}(\sigma^+ / 2) = 4kTy e^{5y/2} (1 - 2y) = -4kTy (1 + y/2) \quad (2.22)$$

where we have retained only terms up to order y^2 , since the second approximation is valid only to this order. In this way, we obtain the equation of state:

$$P/nkT = \exp[4y(1 + y/2)] \quad (2.23)$$

Figure 3 shows the comparison of Eq. (2.23) to the molecular-dynamics results obtained by Alder and Wainwright.⁽³⁾ We find that this second approximation equation of state exhibits quite fine agreement with the molecular-dynamics results up to the Alder transition density. In Table I, we compare our result with accurate virial expansion of Ree and Hoover⁽⁴⁾ and other theories.⁽⁵⁾ It is rather remarkable that our equation of state gives a quite fine agreement up to the sixth virial.

3. SEMIEMPIRICAL EQUATION OF STATE FOR THE HARD-CORE SYSTEM WITH ATTRACTIVE POTENTIAL

Young and Alder⁽⁶⁾ applied the semiempirical equation of state of Carnahan and Starling⁽⁷⁾ to the hard-core systems with attractive tails empirically. It may be interesting to apply our equation of state to these systems as it has a much simpler form.

The contribution of the attractive potentials may well be approximated by van der Waals' attractive term. So we assume that the total pressure is written in an additive form:

$$P = \frac{NkT}{V} e^{4y+2y^2} - \frac{a}{V^2} \quad (3.1)$$

where the first term is our equation of state (2.23) for the hard-sphere system and the second term is van der Waals' attractive term. The critical point is obtained by the equations

$$\left(\frac{\partial P}{\partial V} \right)_T = \left(\frac{\partial^2 P}{\partial V^2} \right)_T = 0 \quad (3.2)$$

These equations are reduced to a form

$$(2y)^3 + 3(2y)^2 + 3(2y) - 1 = 0 \quad (3.3)$$

and it has a simple solution:

$$y_c = (2^{1/3} - 1)/2 = 0.1300 \quad (3.4)$$

and Kamerlingh-Onnes' constant is given by

$$\frac{NkT_c}{P_c V_c} = \frac{2}{2 - (2y_c + 1)^2} e^{-4y_c - 2y_c^2} = 2.787 \quad (3.5)$$

These results are sufficiently close to Young and Alder's values, 0.1304 and 2.786.

4. CONCLUSION

We have presented a method which gives a fairly good prescription to obtain the equilibrium properties of the hard-sphere system and at the same time simple semiempirical solution for the critical point of the hard-core system with attractive potential.

We should note here that there have been other intuitive methods to supply the equations of state for the hard-sphere system. One of these is established by Clausius and Boltzmann.⁽⁸⁾ Their method is founded on the covolume concept. Another is the scaled particle theory by Reiss, Frisch, and Lebowitz.⁽⁹⁾ How do these concepts keep in touch and lose contact with each other inherently? This question arouses a logical interest.

Recently, the author is informed that the distribution near the wall is treated elaborately by the configuration integration method by Percus⁽¹⁰⁾ and others, though they did not derive the equation of state directly from the distribution. The incorporation of our consideration into their treatment may give rise to better results.

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