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Excluded Volume: A Historical Enigma of the van der Waals Equation of State[†]

Anatoly I. Rusanov*

Mendeleev Center, St. Petersburg State University, 199034 St. Petersburg, Russia

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The value of excluded volume taken by van der Waals as the quadruple molecular volume was a subject of discussion for a long time. The enigma of the van der Waals equation of state consists in the fact that it yields a correct result only with an incorrect excluded volume. The paradox has been recently resolved in the author's general theory of an equation of state based on the excluded volume. A short outline of the theory is given with the derivation of the van der Waals equation as corresponding to a linear dependence of the exclusion factor on the packing fraction. The generation of other equations of state is exhibited by example of a system of hard spheres. The novel theory is shown to be potentially important for mixtures with large molecular size ratios.

Introduction

As recently as a quarter of a century ago, I was engaged in editing the Russian language version of the book "Molecular Theory of Capillarity"[1] in close and nice collaboration with the authors, Sir John Rowlinson and Professor Ben Widom. Special attention was then paid to the theory of van der Waals whose works seemed to be of great academic interest for Sir John still earlier.[2,3] At the beginning of the new millennium, I came in touch with the van der Waals equation of state when creating a general theory of equation of state based on excluded volume.[4−7] Concerning van der Waals, two consequences of the theory were of significance: (a) a new and simple way of derivation of the van der Waals equation of state and (b) a clue to a historical enigma contained in the van der Waals equation and related to the excluded volume. Both the aspects seem to be worthy of discussion in the Festschrift devoted to Sir John S. Rowlinson.

Close to 1660, the first equation of state, known as the Boyle−Mariotte law, established the inverse proportionality between the pressure, p, and the volume, V, of a gas

$$pV = \text{a constant} \tag{1}$$

In 1738, Daniel Bernoulli was the first to state that pressure cannot be proportional to density at high pressures and to introduce a volume correction to eq 1. In his famous "Hydrodynamica" (written during his work at the St. Petersburg Academy of Sciences), he derived, on the basis of kinetic theory of fluids, an equation of state as[8]

$$\pi = \frac{1 - m^{1/3}}{s - m^{1/3}s^{2/3}}P \tag{2}$$

where π and P are the final and initial values of the gas pressure when changing the gas volume; s is the volume ratio for the two states; and m is the minimal possible volume (when the gas molecules are in contact with each other) divided by the initial volume. Setting $m \rightarrow 0$ changes eq 2 to eq 1. So, the idea of taking into account the own volume of molecules in an equation of state seems to be very old. In the 19th century, a number of authors introduced volume corrections into an equation of state before van der Waals (the list of them was compiled by Clausius[9]), but only the van der Waals equation of state predicted a phase transition.[10]

The classical format of the van der Waals equation of state is

$$\left(p + \frac{a}{v^2}\right)(v - b) = k_B T \tag{3}$$

where v is volume per molecule; a and b are constants; k_B is the Boltzmann constant; and T is temperature. van der Waals put the constant b (earlier termed as "covolume") to be equal to four times the molecular volume of a gas in question. Taking this into account, we can rewrite eq 3 as

$$p = \frac{k_B T}{v - 4v_0} - \frac{a}{v^2} \tag{4}$$

where v_0 is the intrinsic volume of a single molecule. Concerning his equation of state, van der Waals was anxious to make it more accurate and to explain the coefficient 4 in eq 4. He believed the first problem could be resolved by considering b in eq 3 not as a constant, but as a certain function of density. He tried to find this function but did not succeed in his efforts. Nevertheless, there was a useful consequence of that work as the initiation of computing virial coefficients (which has been in progress up to the present time).

The justification of coefficient 4 was a real headache for van der Waals. By physical meaning, the term $4v_0$ should be an excluded volume, but the latter is equal to $8v_0$. Indeed, if we imagine that a spherical particle of radius r and volume $v_0 = (4/3)\pi r^3$ ceases its movement in a gas and becomes resting, this makes the part of the space of volume

$$v^{ex} = \frac{4}{3}\pi(r + r_1)^3 = (v_0^{1/3} + v_1^{1/3})^3 \tag{5}$$

inaccessible for the centers of particles of radius r_1 and volume v_1 (Figure 1). This is just the excluded volume, and we have $v^{ex} = 8v_0$ at $r_1 = r$. Following this logic, one should replace coefficient 4 in eq 4 by 8. However, this would make eq 4 incorrect in the sense that eq 4 would not reproduce properly the second virial coefficient $B_2 = 4v_0 - a/kT$. Thus, it resulted

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* Corresponding author. E-mail: rusanov@ar1047.spb.edu.

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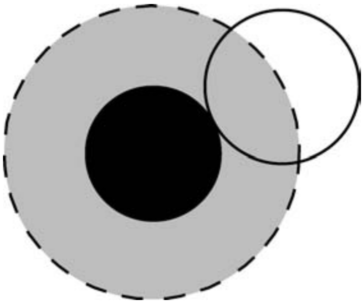

Figure 1. Resting particle (in black) creating the excluded volume (shadowed) with respect to a moving particle.

that the equation of state should include incorrect excluded volume to be correct as a whole, and this was a paradoxical enigma. van der Waals tried to resolve the paradox by arguing that always two particles participate in a collision, and for this reason, 8 should be divided by 2. Looking too artificial, this statement did not explain why and how the excluded volume could be related to the number of colliding particles.

In any case, van der Waals' argument was completely ruined by Planck[11] who derived a correct equation of state with the correct excluded volume. His equation of state for a monatomic gas is

$$p = -\frac{k_B T}{\beta} \ln\left(1 - \frac{\beta}{v}\right) - \frac{\alpha}{v^2} \tag{6}$$

where the constant α is obviously identical with a in eq 4. Expressing his and van der Waals' equations as a power series in $1/v$, Planck found his constant β to be twice as large as that of van der Waals, i.e., $\beta = 8v_0$. With this value, meaning that β is just the excluded volume, eq 6 becomes

$$p = -\frac{k_B T}{8v_0} \ln\left(1 - \frac{8v_0}{v}\right) - \frac{\alpha}{v^2} \tag{7}$$

For better comparison, it is convenient to rewrite eqs 4 and 7 in dimensionless forms as

$$\tilde{p} = \frac{\varphi}{1 - 4\varphi} - \tilde{a}\varphi^2 \text{ (van der Waals)} \tag{8}$$

$$\tilde{p} = -\frac{\ln(1 - 8\varphi)}{8} - \tilde{a}\varphi^2 \text{ (Planck)} \tag{9}$$

where $\tilde{p} \equiv pv_0/k_B T$, $\varphi \equiv v_0/v$ is the packing fraction, and $\tilde{a} \equiv a/k_B T v_0 = \alpha/k_B T v_0$ is a dimensionless form for the attractive constant.

Both eqs 8 and 9 yield the proper values for the first and second coefficients of the virial expansion

$$\tilde{p} = \varphi + (4 - \tilde{a})\varphi^2 + \cdots \tag{10}$$

and Planck modestly wrote that he only confirmed the van der Waals equation. Strictly speaking, however, eqs 8 and 9 are different relationships, and the first question to be put is: which of the equations is more accurate? Using the virial equation of state, one can easily determine the van der Waals equation as a more exact relationship. This makes the enigma of this equation still less understandable. Indeed, how it can happen that an equation with an incorrect excluded volume is more accurate than an equation with the correct one? This enigma was a challenge for theory for many years after van der Waals and has been relatively recently resolved within the frames of the above-mentioned general theory of equation of state based on excluded volume.[4−7] So, to proceed to further discussion, we have to outline the theory itself.

Master Equation

The central idea of the theory is the derivation of a master equation as a rigorous relationship capable of generating equations of state. The starting point is an abecedarian expression for chemical potential given by statistical mechanics

$$\mu_i = \mu_i^0 + k_B T \ln(c_i \Lambda_i^3) \tag{11}$$

where μ_i and μ_i^0 are the chemical potentials of a moving and resting molecule of the ith species in a given multicomponent system; c_i and Λ_i are the concentration (the molecular number density) and thermal de Broglie wavelength of the ith species, respectively. A molecule with resting center of mass behaves, in all other respects, in an ordinary way and, naturally, interacts with other (both moving and resting) molecules of the system, so that the activity coefficient term $k_B T \ln f_i$ has been incorporated in μ_i^0. Because of the last quantity, operating thermodynamically with eq 11 requires the knowledge of not only ordinary thermodynamics but also the thermodynamics of systems with resting molecules. Such thermodynamics is formulated quite similarly and with same the relationships[4] but with different numerical values of quantities. For example, ordinary thermodynamics relates chemical potential to pressure (at fixed temperature and composition) as

$$d\mu_i = v_i dp \tag{12}$$

where v_i is the partial molecular volume of the ith species. For a molecule with resting center of mass, we have a similar relationship

$$d\mu_i^0 = v_i^0 dp \tag{13}$$

A partial molecular volume is defined as a change of the system volume necessary for restoring the initial value of pressure after adding a single molecule of a given species to the system. Since a resting molecule does not contribute to the kinetic part of pressure, a change in volume to restore the initial pressure after adding a resting molecule should be different from that after adding a moving molecule, i.e., $v_i^0 \neq v_i$. Depending on the play of interactions, the partial molecular volume of a resting molecule can be of any sign but is positive and reduced to the excluded volume in the absence of long-range forces. So, a rigorous thermodynamic definition of the excluded volume v_i^{ex} for the ith species can be formulated as

$$v_i^{ex} \equiv v_i^0|_{\text{no long-range forces}} \tag{14}$$

Returning now to eq 11, we differentiate it at fixed temperature and composition and substitute eq 13 to obtain

$$d\mu_i = v_i^0 dp + kTd \ln c_i \tag{15}$$

(Λ_i^3 is eliminated as a function of merely temperature). At fixed temperature and composition, the Gibbs−Duhem equation reads

$$dp = \sum_i c_i d\mu_i \tag{16}$$

and, after substituting eq 15, can be written in the form

$$\frac{dp}{dc} = \frac{k_B T}{1 - cv^0} \tag{17}$$

where $c \equiv \sum_i c_i$ is the total concentration of all species in the system; $v^0 \equiv \sum_i x_i v_i^0$ is the average (with respect to various species) value of the partial molecular volume of a resting molecule; and x_i is the mole fraction of the ith species (a given fixed quantity in our consideration).

For the part of pressure p' originating from short-range (repulsive) forces (when the partial molecular volume is replaced by the excluded volume), we can rewrite eq 17 as

$$\frac{dp'}{dc} = \frac{k_B T}{1 - cv^{ex}} \tag{18}$$

where $v^{ex} \equiv \sum_i x_i v_i^{ex}$ is the average excluded volume per molecule. The integration of eq 18 yields

$$p' = k_B T \int_0^c \frac{dc}{1 - cv^{ex}} \tag{19}$$

which shows that $v^{ex}(c)$ is the only function that is needed for finding p'. Then the total pressure is

$$p = k_B T \int_0^c \frac{dc}{1 - cv^{ex}} + p'' \tag{20}$$

where p'' is the long-range part of pressure. If, in particular, the van der Waals approach is used for p'', eq 20 takes the form

$$p = k_B T \int_0^c \frac{dc}{1 - cv^{ex}} - \sum_{i,k} a_{ik} c_i c_k \tag{21}$$

Equation 20 is just the master equation of the excluded volume theory of a three-dimensional equation of state. Proceeding to the above dimensionless variables, eqs 20 and 21 become

$$\tilde{p} = \int_0^{\varphi} \frac{d\varphi}{1 - \varphi f} + \tilde{p}'' \tag{22}$$

$$\tilde{p} = \int_0^{\varphi} \frac{d\varphi}{1 - \varphi f} - \sum_{i,k} \tilde{a}_{ik} \varphi_i \varphi_k \tag{23}$$

where $\varphi \equiv \sum_i \varphi_i$ is the total packing fraction of all species; $f \equiv v^{ex}/v_0$ is the exclusion factor; and $\tilde{a}_{ik} \equiv a_{ik} v_0 / k_B T v_{i0} v_{k0}$ is a dimensionless form for the van der Waals attraction constant ($v_0 \equiv \sum_i x_i v_{i0}$ being the average molecular volume).

In a similar way, one can construct the master equation for two-dimensional pressure Π by replacing molecular volume v_0 with molecular parking area a_0, excluded volume v^{ex} with excluded area a^{ex}, bulk concentration c with surface concentration Γ, etc. However, this changeover is not so trivial as it can seem to be. For a surface monolayer with anisometric molecules (which is typical, e.g., for surfactant monolayers), the equation of state looks even more complicated than in the three-dimensional case because parking area and excluded area are dependent not only on molecular size but also on molecular orientation. As a consequence, a rigorous theory of the equation of state for a surface monolayer should be formulated within the frames of a three-dimensional approach[6] by introducing molecular size h_i in the normal direction and the quantity

$$h \equiv \sum_i x_i h_i \tag{24}$$

as the average monolayer thickness. The resulting master equation for a surface monolayer is

$$\Pi = k_B T \int_0^{\Gamma} \frac{1 - d \ln h / d \ln \Gamma}{1 - \Gamma a^{ex}} d\Gamma + \Pi'' \tag{25}$$

and requires, for its integration, the knowledge of two functions: $a^{ex}(\Gamma)$ and $h(\Gamma)$. The second function refers to the problem of an orientation equation of state and is interesting itself.

Since variables h and Γ change in the same direction (surface molecules become more and more "standing" as surface concentration increases), we have $d \ln h / d \ln \Gamma > 0$. If this derivative is sufficiently large (and remembering that the long-range part of two-dimensional pressure Π'' is negative), the whole right-hand side of eq 25 can become negative to cause the condition $d\Pi/d\Gamma < 0$, which means instability and a two-dimensional phase transition. Thus, we see that, still without an equation of state, the master equation itself predicts the possibility of a two-dimensional phase transition induced by surface orientation. If only molecules of high symmetry are contained in a surface monolayer and the effect of orientation is absent, we have $d \ln h / d \ln \Gamma = 0$, and eq 25 is reduced to

$$\Pi = k_B T \int_0^{\Gamma} \frac{d\Gamma}{1 - \Gamma a^{ex}} + \Pi'' \tag{26}$$

which is the master equation for the pure two-dimensional case and a direct analogy of eq 20.

Returning now to the three-dimensional case, we will consider in detail the exclusion factor to exhibit an advantage of the excluded volume approach in the theory of equation of state.

Exclusion Factor

Equation 5 operates with free molecules in the absence of clusterization when the system under consideration is a rarified gas. Denoting for this case the excluded volume as v_0^{ex} and the exclusion factor value as f_0, we have, according to eq 5, $f_0 \equiv v_0^{ex}/v_0 = 8$ not only for a one-component system but also for a mixture provided molecules of different species are equal in size. If, however, molecules of different species are different in size, f_0 is an object for computation. The computational scheme is a simple generalization of eq 5

$$f_0 = \frac{v_0^{ex}}{v_0} = \frac{\sum_{i,k} x_i x_k (v_{i0}^{1/3} + v_{k0}^{1/3})^3}{\sum_i x_i v_{i0}} \tag{27}$$

Comparing eq 27 with similar formulas for the second virial coefficient confirms that f_0 is equal to the reduplicate dimensionless second virial coefficient $b_2 \equiv B_2/v_0$ for a mixture of hard spheres. Thus, finding f_0 is practically reduced to finding the second virial coefficient b_2 whose computational technique has been well developed and makes no problems. Generally, one can say f_0 depends both on composition and on molecular size difference and is smaller for a mixture than for pure components. For a binary mixture, the dependence of f_0 on the mole fraction x is characterized by a minimum whose deepness increases with the molecular size difference. The limiting minimum value is $2 + 6x$ so that $f_0 > 2$ in any case.[5]

We now turn to the central problem of an equation of state, the dependence of f^{ex} on density at given composition and molecular size difference, which is caused by clusterization. Taking the second form of eq 5 (which is applicable even to nonspherical particles provided they are similar in shape), the excluded volume V^{ex} created by a cluster of volume V_c with respect to a single molecule of the kth species of volume v_{k0} is

$$V^{ex} = (V_c^{1/3} + v_{k0}^{1/3})^3 \tag{28}$$

If the cluster totally contains n molecules of various species, the average volume per molecule in the cluster is $v_c \equiv V_c/n$ to modify eq 28 to

$$V_k^{\mathrm{ex}} = [(nv_{\mathrm{c}})^{1/3} + v_{k0}^{1/3}]^3 \tag{29}$$

The average excluded volume created by the cluster with respect to all species is

$$V^{\mathrm{ex}} = \sum_k x_k[(nv_{\mathrm{c}})^{1/3} + v_{k0}^{1/3}]^3 \tag{30}$$

or, if taken per one particle

$$v^{\mathrm{ex}} = V^{\mathrm{ex}}/n = \sum_k x_k[v_{\mathrm{c}}^{1/3} + (v_{k0}/n)^{1/3}]^3 \tag{31}$$

Correspondingly, the exclusion factor is expressed as

$$f = \frac{v^{\mathrm{ex}}}{v_0} = \sum_k x_k[(v_{\mathrm{c}}/v_0)^{1/3} + (v_{k0}/nv_0)^{1/3}]^3 \tag{32}$$

Both v_0 and v_{c} are average quantities. However, v_0 depends only on composition, whereas volume v_{c} depends, in addition, on the cluster size because of surface effects and takes a constant value (let it be $\bar{v}_{\mathrm{c}}$) only in the macroscopic limit $n \to \infty$ (at a fixed composition). Correspondingly, the exclusion factor tends to the limit $\bar{v}_{\mathrm{c}}/v_0$, and we may write the general condition

$$f_0 \geq f \geq \bar{v}_{\mathrm{c}}/v_0 \tag{33}$$

for a multicomponent system. Generally, the ratio $\bar{v}_{\mathrm{c}}/v_0$ is determined by the type of packing of molecules in a cluster. Since hard spheres are unable to fill the space without cavities, the ratio $\bar{v}_{\mathrm{c}}/v_0$ for hard spheres is larger than unity, although it can approach unity due to filling cavities between larger spheres by smaller ones.

In the case of a one-component system, eq 32 takes the form

$$f = [(v_{\mathrm{c}}/v_0)^{1/3} + n^{-1/3}]^3 \tag{34}$$

and the condition expressed in eq 33 becomes

$$8 \geq f \geq \bar{v}_{\mathrm{c}}/v_0 \tag{35}$$

Applied to hard spheres, eq 35 yields

$$8 \geq f \geq 6/\pi \approx 1.91 \text{ (cubic packing)} \tag{36}$$

$$8 \geq f \geq 6/\pi\sqrt{2} \approx 1.35 \text{ (hexagonal packing)} \tag{37}$$

Here we see a remarkable property of the exclusion factor, changing within a very narrow range when pressure varies from zero to infinity. One may say the change of the exclusion factor is practically negligible as compared with the change of pressure. This property is especially useful for constructing an equation of state in the situation when the problem of finding an exact function $f^{\mathrm{ex}}(c)$ has not yet been solved. We will illustrate this with some examples.

Generation of Equations of State

Let us now see how eq 22 or 23 can generate equations of state. Since we deal with the short-range part of pressure (which we denoted as p' in eq 18), we here retain only the first part of eq 22 or 23 as

$$\tilde{p}' = \int_0^{\varphi} \frac{\mathrm{d}\varphi}{1 - \varphi f} \tag{38}$$

To take the integral in eq 38, one has to know the $f(\varphi)$ function. This function has not yet been found in theory, but we showed above that the exclusion factor f is capable of variation only within a narrow range of several units. This allows us to hope that simple assumptions or a single fitting parameter in case of need can secure the useful work of eq 38 unless an exact form of $f(\varphi)$ is found.

Zero Approximation. Since, as was stated above, the relative change in f is negligible as compared with a change in pressure, the simplest assumption that we can make is setting f a constant. Then, eq 38 yields

$$\tilde{p}' = -\frac{\ln(1 - \varphi f)}{f} \tag{39}$$

We qualify this case as the zero approximation. With a specified value of f, eq 39 can be valid, within a small region of φ, for an arbitrary part of the isotherm including a condensed state of matter. In the particular case of a rarified gas, we have to set $f = f_0$, and eq 39 becomes

$$\tilde{p}' = -\frac{\ln(1 - \varphi f_0)}{f_0} \tag{40}$$

where f_0 is calculated according to eq 27. Substituting eq 40 in eq 23 leads to the relationship

$$\tilde{p} = -\frac{\ln(1 - \varphi f_0)}{f_0} - \sum_{i,k} \tilde{a}_{ik}\varphi_i\varphi_k \tag{41}$$

that can be called the generalized Planck equation of state for a multicomponent gaseous mixture. In the particular one-component case with $f_0 = 8$, eq 41 changes to the classical Planck equation for a monatomic gas (cf. eq 9). We now can say the Planck equation corresponds to the zero approximation of the excluded volume theory of an equation of state. Since a logarithm can exist only for positive quantities, eq 41 loses its physical sense beyond the range $\varphi < 1/f_0$ or $\varphi < 1/8$ for the one-component case. The practical range is much narrower for eq 41 because the exclusion factor value in this equation refers to the limiting case of a rarified gas. For this reason, any attempt of using the Planck equation for predicting a phase transition looks unjustified.

First Approximation. Let us now consider f as a variable quantity depending on φ and take the state of a rarified gas with the exclusion factor value f_0 for the initial state. Since the simplest form is a linear dependence, we may write, as the first approximation

$$f = f_0 - k\varphi \tag{42}$$

where k is a positive constant. The sign "minus" in eq 42 corresponds to the estimations given in eqs 35 to 37 and shows that the exclusion factor decreases with increasing packing fraction. Putting eq 42 in eq 38 yields

$$\tilde{p}' = \int_0^{\varphi} \frac{\mathrm{d}\varphi}{1 - f_0\varphi + k\varphi^2} \tag{43}$$

The form of a function resulting from the integration in eq 43 depends on an ascribed value of the coefficient k and can include cumbersome relationships. The excluded volume theory of an equation of state selects a simplest solution at every stage (this principle is known in science as Ockham's razor). In the case of eq 43, the simplest result corresponds to the value $k = (f_0/2)^2$ to give

$$\tilde{p}' = \frac{\varphi}{1 - (f_0/2)\varphi} \tag{44}$$

Substituting eq 44 into eq 23 results in the relationship

$$\tilde{p} = \frac{\varphi}{1 - (f_0/2)\varphi} - \sum_{i,k} \tilde{a}_{ik}\varphi_i\varphi_k \tag{45}$$

which can be called the generalized van der Waals equation of state for a fluid mixture. Passing to the one-component case

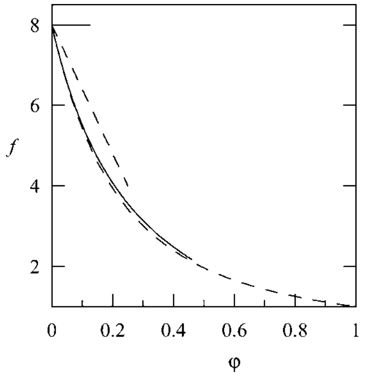

Figure 2. Dependence of the exclusion factor f on the packing fraction φ in the case of the Planck equation (the upper solid line), the van der Waals equation (the upper dash line), eq 51 (the lower solid line), and the virial equation of state for hard spheres with ten first terms retained (the lower dash line).

and setting $f_0 = 8$, eq 45 is reduced to the classical van der Waals equation (eq 8). To secure a positive value for pressure, eq 45 cannot be used beyond the range $\varphi < 2/f_0$ even for the case of hard spheres, which makes $\varphi < 1/4$ for a one-component system. So we see that the van der Waals equation is not only more exact and stands higher in the hierarchy of approximations but also possesses a wider action range as compared with the Planck equation.

The above derivation discloses the historical enigma of the van der Waals equation. We now can explain it as follows. (a) It is true that parameter b in eq 3 originates from the excluded volume, but b itself is not the excluded volume. The constancy of b does not mean that the excluded volume is constant. (b) The van der Waals equation accounts for the dependence of the excluded volume on the fluid density, and just this dependence causes b to be different from the excluded volume. (c) The particular value $b = 4$ corresponds to the linear dependence of the exclusion factor on the packing fraction.

Second Approximation. Although the aim of the article, the explanation of the historical enigma of the van der Waals equation, has been attained, we continue our consideration to complete the outline of the theory. To choose a function $f(\varphi)$ for the second approximation, we should have a general conception of this dependence. This can be easily attained with an example of equal hard spheres from the dimensionless virial expansion $\tilde{p} = \sum_{i\geq 1} b_i\varphi^i$ as[4]

$$f(\varphi) = \sum_{i\geq 2} ib_i\varphi^{i-1}/\varphi\left(1 + \sum_{i\geq 2} ib_i\varphi^{i-1}\right) \qquad (46)$$

Truncating the virial expansion after the first ten terms and using the numerical values for the first ten dimensionless virial coefficients,[4] we obtain the $f(\varphi)$ dependence as a slightly concave descending curve (Figure 2). To reflect the concavity, we modify eq 42 as

$$f = \frac{f_0 - k_1\varphi}{1 + k_2\varphi} \qquad (47)$$

The coefficients k_1 and k_2 should satisfy the requirements $f = f_0$ and $df/d\varphi = -K$ at $\varphi = 0$ where $K = 4b_2^2 - 3b_3$ according to eq 46. We then have $k_1 = K - f_0k_2$ so that only one of the two coefficients k_1 and k_2 can vary independently. After substituting eq 47 in eq 38, the simplest result of integration corresponds to the values $k_1 = (f_0 - K^{1/2})^2$ and $k \equiv k_2 = 2K^{1/2} - f_0$ and looks as[5]

$$\tilde{p}' = \left(1 + \frac{k}{\beta}\right)\frac{\varphi}{1 - \beta\varphi} + \frac{k}{\beta^2}\ln(1 - \beta\varphi) \qquad (48)$$

where $\beta \equiv (f_0 - k)/2$. The constants k and β are related to the second and third dimensionless virial coefficients as follows

$$k = 2b_2\left[2\left(1 - \frac{3b_3}{4b_2^2}\right)^{1/2} - 1\right] \qquad (49)$$

$$\beta = 2b_2\left[1 - \left(1 - \frac{3b_3}{4b_2^2}\right)^{1/2}\right] \qquad (50)$$

Equation 48 represents the second approximation of the excluded volume theory of an equation of state. For a one-component system, we have $f_0 = 8$ and $K = 34$. Using these values represents eq 48 in the numerical form

$$\tilde{p}' = 2.688\frac{\varphi}{1 - 2.169\varphi} + 0.778\ln(1 - 2.169\varphi) \qquad (51)$$

with the allowable action range $\varphi < 0.461$. Comparing this with the ranges for eqs 40 and 44, we see that ascending in the hierarchy of approximations not only makes an equation of state more accurate but also widens its applicability range. Figure 2 shows the behavior of the exclusion factor in the case of the Planck equation (the zero approximation of the excluded volume theory of an equation of state), van der Waals equation (the first approximation), and eq 51 (the second approximation) as compared with the above-mentioned function $f(\varphi)$ corresponding to the virial equation of state for hard spheres (almost the same function corresponds to the Carnahan−Starling equation that originates from the virial equation of state). Curve 3 is seen to be very close to curve 4, which shows the advantage of eq 51. However, all three equations of state refer to relatively low-density systems of hard spheres and cannot be applied to the entire density range.

Higher Approximations for the Entire Density Range. In the above approach, we stuck to the virial expansion to estimate numerical values of coefficients. This method, however, is inapplicable to dense systems. In this case, a precise computer simulation database can be an alternative to the virial expansion. The excluded volume theory of an equation of state gives the following expression for the compressibility factor $Z \equiv \tilde{p}'/\varphi$ of a system of mixed hard spheres or disks

$$Z^{(n)} = \frac{1}{(1 - k\varphi)^{n-1}}\left\{1 + \frac{f_0 - 2k(n-1)}{(n-1)(n-2)k^2\varphi} \times \left[(1 - k\varphi)^{n-1} - 1 + (n-1)k\varphi\right]\right\} \quad (n > 2) \qquad (52)$$

where n is the approximation number and k is a free parameter. Equation 52 yields proper values for the first and second virial coefficients irrespective of the value of k so that k can be easily used as a fitting parameter for the entire density range. Good results were obtained using the databases by Alder and Wainwright[12] and by Erpenbeck and Wood[13] for hard spheres and the database of Erpenbeck and Luban[14] for hard disks, and a number of famous equations of state were reproduced with the aid of eq 52 ascending to a very precise relationship in the seventh approximation (with the coefficient of determination up to 0.999998).[6,7] Of course, the usage of a fitting procedure does not beautify a theory. However, if we remember that modern equations of state can include ten or more fitting parameters, the use of a single fitting parameter to cover almost

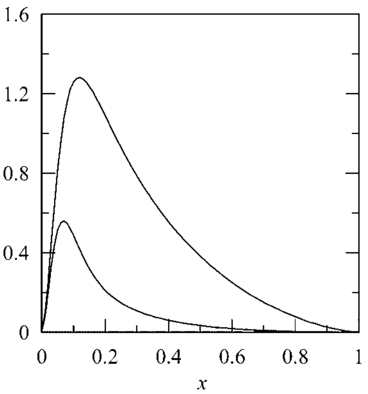

Figure 3. Dependence of coefficients y_1 (the upper curve) and y_2 (the lower curve) of eq 53 on the mole fraction $x \equiv x_2$ at the size ratio $d_2/d_1 = 5$.

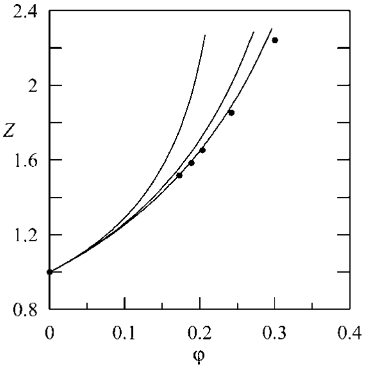

Figure 4. Isotherms of the compressibility factor Z for a binary mixture of hard spheres at $d_2/d_1 = 5$ and $x(\equiv x_2) = 0.064$ in the zero (the generalized Planck equation, the left curve), first (the generalized van der Waals equation, the middle curve), and second (eq 48, the right curve) approximations of the excluded volume theory of an equation of state. The points represent the database of Enciso et al.[17]

ideally 14 database points is unique and gives evidence of the high quality of an equation of state itself.

Concerning a system of hard spheres of equal size, eq 52 is capable of exhibiting a higher accuracy than the Carnahan–Starling equation, but this advantage cannot be of significance because the Carnahan–Starling equation is already very accurate itself. We have another situation for hard-sphere mixtures. Mansoori et al.[15] generalized the Carnahan–Starling equation for an arbitrary mixture of hard spheres as

$$Z = \frac{1 + \varphi + \varphi^2 - 3\varphi(y_1 + y_2\varphi) - y_3\varphi^3}{(1 - \varphi)^3} \tag{53}$$

where coefficients y_1, y_2, and y_3 were given as functions of the diameters d_i and mole fractions x_i of hard spheres. Equation 53 was found to be in excellent agreement with results of Monte Carlo simulation of equimolar binary mixtures of hard spheres at $d_2/d_1 = 1.1$ and $d_2/d_1 = 5/3$.[15] However, a subsequent test by Jackson, Rowlinson, and van Swol[16] showed significant deviations at high densities and large size ratios (up to 20). It is of note that the concentration range is also important for such tests. Similarly to the second and third virial coefficients, coefficients y_1, y_2, and y_3 in eq 53 are sensitive to concentration in a binary system with a large size ratio, especially at a small concentration of a species with a larger molecular size. Figure 3 exhibits the existence of sharp maxima of coefficients y_1 and y_2 at a small concentration of component 2 in a binary mixture of hard spheres at $d_2/d_1 = 5$. In this concentration range, positive values of y_1 and y_2 are considerably larger than at the equimolar composition and can spoil the dependence Z on φ up to the reversal in sign, which makes eq 53 out of physical sense.

The database by Enciso et al.[17] for a binary mixture of hard spheres with $d_2/d_1 = 5$ and $x_2 = 0.064$ makes a good testing ground for equations of state. In spite of a small mole fraction of larger spheres, the properties of the system differ significantly from those of a pure component. For example, the dimensionless second and third virial coefficients are $b_2 \approx 2.07$ as compared with 4 and $b_3 \approx 3.77$ as compared with 10 for spheres of equal size.[18,19] For the above reason, eq 53 does not work in this case. However, eq 52 encounters no problems. Preliminarily, we can use the above values of b_2 and b_3 for constructing the zero (the generalized Planck equation), first (the generalized van der Waals equation), and second (eqs 48–50) approximations of the excluded volume theory of an equation of state. The result is shown in Figure 4, and we see that already the second approximation corresponds reasonably well to the database of Enciso et al. that refers to a sufficiently low concentration range. As for eq 52, it produces the best result in the fourth approximation as[18,19]

$$Z^{(4)} \approx \frac{1 - 1.283\varphi + 0.478\varphi^2}{(1 - 1.117\varphi)^3} \tag{54}$$

which is a high-precision equation of state with respect to the database (the coefficient of determination is 0.999677, and the average deviation is 0.26 %). Of course, it would be interesting to test eq 52 for a binary system with the molecular size ratio 20, but the computer simulation database obtained by Jackson, Rowlinson, and van Swol[16] was not published in a numerical form.

Conclusion

The excluded volume theory of an equation of state supplies a detailed explanation of the historical enigma of the van der Waals equation of state. The central point of understanding is the proof of the fact that the constancy of van der Waals' constant b does not mean the constancy of the excluded volume. The particular constant value $b = 4v_0$ has been also proved as corresponding to the linear dependence of the exclusion factor on the packing fraction.

The theory itself needs further development to be complete. In fact, the dependence of the clasterization degree on the fluid density is required. This is a global problem of the whole theory of fluids, which remains unsolved up to the present time in spite of the efforts of many investigators. However, even in its present form, the excluded volume theory of an equation of state can be useful for finding numerical equations of state for mixtures of hard spheres with a significant size difference.

One more idea was suggested by the reviewer of this article and concerns the estimation of an asymmetry of the phase coexistence curve near the critical point. The method was proposed by Wang and Anisimov and tested with the use of various equations of state.[20] However, since the estimation requires only derivatives of the chemical potential with respect to density and temperature (not the chemical potential value itself), it would be more rational and rigorous to use directly the above master equation (eq 17). In an important case of week interactions and a large molecular size, eq 17 is substituted by eq 18 with the excluded volume. This makes the excluded volume a quantity directly contributing to the binodal asymmetry in fluid criticality.

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