Russian Chemical Reviews **74** (2) 117 – 127 (2005) © 2005 Russian Academy of Sciences and Turpion Ltd

DOI 10.1070/RC2005v074n02ABEH000970

Novel approach to the equation of state for fluid systems, based on the concept of the exclusion factor

A I Rusanov

Contents

I.	Introduction	117
II.	The equation of state for bulk phases	118
III.	Equation of state for surface monolayers	122
IV.	The orientation equation of state	125
V.	Conclusion	126

Abstract. The review summarises the achievements in the theory of the equation of state. Novel approaches and new high-precision equations of state for one- and multicomponent fluid systems are consdidered. The results are given for both bulk phases and surface monolayers including two-dimensional equations. In the framework of the theory based on the exclusion factor, a hierarchy of approximations is formulated, incorporating both well-established and relatively new equations of state. The bibliography includes 79 references.

I. Introduction

A physicochemical state of matter is characterised by some state parameters such as temperature, pressure, density and chemical composition. The significance of the equation of state consists in that it relates these parameters to one another (usually, in explicit form). Finding the equation of state is one of the central problems of the knowledge of matter, which has been under discussion in the scientific literature since 1662 (the Boyle – Mariotte law). Research on the properties of gases took two centuries but the search for a general equation of state for gases and fluids began only after proposal of the idea of continuous transition from gas to fluid (van der Waals, 1873). Interest in this problem is unabated so far. To date, a great body of experimental data has been accumulated. Complete histories of the first fifty equations of state are known [1] but it is impossible to count the total number of the equations of state proposed. The matters in hand are various types (cubic, logarithmic, *etc*. equations), models (*e.g*., lattice models) and aspects of the equation of state, which have been the subject of particular reviews. The results obtained in this field by the end of the twentieth century are summarised in an incomplete collection of such reviews.[2] The present review is devoted to the major aspect of the equation of state, namely, the use of the concept of the exclusion factor (excluded volume or surface area).

The first equations of state for fluids were based on the Boltzmann and van der Waals concepts of excluded volume, *i.e*., the volume that must be subtracted from the actual volume of a system due to the fact that particles in the system have their own volumes. It is easy to understand that in an ideal gas a spherical particle of radius r and volume $\upsilon_0 = 4\pi r^3/3$ creates an excluded (inaccessible to the centres of other identical particles) volume $\upsilon^{ex} = 4\pi(2r)^3/3 = 8\upsilon_0$. Now if we write the van der Waals equation

$$p = \frac{k_B T}{\upsilon - 4\upsilon_0} - \frac{\alpha}{\upsilon^2}, \qquad (1)$$

(p is the pressure, k_B is the Boltzmann constant, T is temperature, υ is the volume per gas particle, α is the attraction constant), we surprisingly see the coefficient 4 instead of 8, which contradicts van der Waals' idea. Replacement of the numerical factor 4 by 8 in this equation leads to an incorrect value of the second virial coefficient. Van der Waals tried to avoid this contradiction by assuming that collisions always occur between two molecules. This argumentation is no longer valid after Planck's equation of state.[3]

$$p = -\frac{k_B T}{8\upsilon_0}\ln\left(1 - \frac{8\upsilon_0}{\upsilon}\right) - \frac{\alpha}{\upsilon^2}, \qquad (2)$$

which contains the excluded volume $8\upsilon_0$ in explicit form. Undoubtedly, Eqns (1) and (2) are different equations of state. But even Planck who expanded the logarithm in a series thought that he confirmed the van der Waals equation which dominated over many decades and was in essence treated as a law of nature; parameters of this equation for particular substances were published in handbooks as physical constants.

The late 1950s and early 1960s were the period when the statistical theory of scaled particles [4, 5] was created and methods of computer simulation (molecular dynamics) of the equation of state were elaborated.[6] The new theory provided much more accurate equations of state, introduced a number of additional geometric notions (*e.g*., the notion of accessible volume, which is immediately related to the equation of state). Over the years it has become a broad field which was called by Reiss (creator of the theory) statistical geometry.[7 – 12] Elaboration of methods of computer simulation permitted experiments with exactly the same models for which theory was created. By the early 1980s research on the equations of state reached a stage of steady rework, refinement and generalisation. The subject of most recent publications is generalisation of the equations of state for multicomponent systems [13 – 24] or modelling of systems comprised of aspherical particles.[25]

A I Rusanov St Petersburg State University, Mendeleev Centre, Universitetskaya nab. 7/9, 199034 St Petersburg, Russian Federation. Fax (7-812) 428 69 39, tel. (7-812) 323 41 20, e-mail: rusanov@AR1047.spb.edu

Received 17 April 2004
Uspekhi Khimii **74** (2) 126 – 137 (2005); translated by A M Raevskiy

The two-dimensional van der Waals equation

$$\Pi = \frac{k_B T}{a - 2a_0} - \frac{\alpha}{a^2} \tag{3}$$

[Π is two-dimensional pressure; a is the surface area per particle; a_0 is the parking area of the particle; the attraction constant, α, is of course different from that which appeared in Eqn (1)] has dominated since the mid-20th century, as follows from a well-known monograph by de Boer,[26] which is to a great extent based on this equation. However, the scaled particle theory also provided more accurate equations in this field (they are given below). In addition, experimenters working with dense surfactant monolayers began using the logarithmic Frumkin equation (at $\alpha = 0$, it is known as the van Laar equation)

$$\Pi = -\frac{k_B T}{a_\infty} \ln\left(1 - \frac{a_\infty}{a}\right) - \frac{\alpha}{a^2}, \tag{4}$$

where a_∞ is the surface area per particle at the maximum degree of coverage of the monolayer. Initially, the van Laar equation [27] and recently also the Frumkin equation [28, 29] were extended to multicomponent systems.

A reference database for the two-dimensional equation of state for hard disks was created (using the molecular dynamics method and Monte Carlo simulation [30]) twenty-five years later than for the three-dimensional equation of state for hard spheres, being, however, characterised by the highest accuracy (0.01%). The last decade was a period of continuous research in the field of computer simulation [31–33] of two-dimensional systems and, as a supplement, of the scaled particle theory.[34] The availability of the high-accuracy database gave impetus to the development of the theory of the two-dimensional equation of state. Quite accurate but rather complex equations (*e.g.*, the Padè and Levin approximants [30]) based on a set of initial virial coefficients were derived. At the same time it was demonstrated that at present derivation of simple and accurate equations for hard disks [35, 36] using the Boltzmann concepts presents no significant difficulties.

Recently, a new approach has been elaborated to the theory of the equation of state based on the exclusion factor (excluded volume or surface area) for both bulk [37–46] and surface [47–54] systems. The approach is based on new thermodynamic relations and on a general relation of statistical mechanics for the chemical potential of a particle (molecule, ion or nanoparticle) of the ith component rather than the scaled particle theory

$$\mu_i = \mu_i^0 + k_B T \ln(c_i \Lambda_i^3), \tag{5}$$

where μ_i^0 is the chemical potential of the particle with centre of mass at rest, c_i is the concentration (particle number per unit volume) and Λ_i is the average de Broglie wavelength (temperature function). A traditional term including the activity coefficient is allowed for by the quantity μ_i^0, which differs from μ only in that it corresponds to the particle at rest.

The main parameter of the new theory is the exclusion factor (reduced excluded volume or surface area) determining the solution to the master equation that generates the equations of state. This parameter varies over a narrow range, thus providing a good accuracy of solution in different approximations. The adequacy of the approach is quite surprising. Not only does the method allow new accurate and simple (the simplicity condition is included in the computational algorithm) equations of state to be derived but it also permits reproduction of known equations that are seemingly not interrelated and establishment of some hierarchy of approximations involving these equations. On the one hand, this permits better understanding of conventional relations (we will see it below taking the van der Waals and Planck equations as examples). On the other hand, this provides a way to systematise the most important available data on the equation of state. Because of this, in the text below we use the formalism of the new approach.

II. The equation of state for bulk phases

Now we introduce some notions and definitions used in the new theory. First of all, this is a new and rigorous thermodynamic definition of the excluded volume υ_i^{ex} as the partial volume of a particle of component i with a resting centre of mass in the absence of all interactions except for the short-range interactions related to the volume of the own particle

$$\upsilon_i^{ex} \equiv \upsilon_i^0 \equiv \left(\frac{\partial V}{\partial N_i^0}\right)_{T, p, N_j, N_{j\neq,1}^0}. \tag{6}$$

Here υ_i^0 is the partial volume of a resting particle of component i defined as the derivative of the system volume V with respect to the number, N_i^0, of particles at rest in the system provided that the temperature, pressure and the numbers, N_j, $N_{j\neq 1}^0$, of other particles are constant. A similar definition of the partial volume, υ_i, of ordinary (moving) particles known in thermodynamics obeys the relationship

$$\upsilon_i = \left(\frac{\partial \mu_i}{\partial p}\right)_{T, \{x_i\}}, \tag{7}$$

where $\{x_i\}$ is the set of mole fractions x_i symbolising the constancy of composition. An analogous expression for particles at rest

$$\upsilon_i^0 = \left(\frac{\partial \mu_i^0}{\partial p}\right)_{T, \{x_i\}}, \tag{8}$$

was derived as a new thermodynamic relation.[38] For both resting and moving particles the partial volume differs from the own particle volume υ_{i0}. For instance, in gases υ_i is incomparably larger than υ_{i0}. Moreover, in contrast to the own particle volume, the partial particle volume can be of any sign because of competition between attractive (long-range) and repulsive forces. In the absence of long-range forces the partial volume of a particle at rest is positive and equals the excluded volume. The excluded volume is always positive, being comparable with the own particle volume. Indeed, the excluded volume is usually treated as a space inaccessible to the centres of mass of moving particles. Assuming particles to be spherical (because of Brownian rotation or simply as a model) and their concentration to be low (rarefied gas), the excluded volume can be estimated as follows. For mobile particles of the kth component of radius r_k, a resting particle of component i of radius r_i creates an excluded volume υ_{ik}^{ex} in the form of a sphere of radius $r_i + r_k$ (Fig. 1). From here it follows

$$\upsilon_{ik}^{ex} = \left(\upsilon_{i0}^{1/3} + \upsilon_{k0}^{1/3}\right)^3, \tag{9}$$

where $\upsilon_{i0} = 4\pi r_i^3/3$ and $\upsilon_{k0} = 4\pi r_k^3/3$ are the corresponding particle volumes [for particles of the same size relationship (9) gives $\upsilon^{ex} = 8\upsilon_0$, as mentioned above]. Averaging of relation (9) gives the excluded volume for a gas mixture

$$\upsilon^{ex} = \sum_{i,k} x_i x_k \left(\upsilon_{i0}^{1/3} + \upsilon_{k0}^{1/3}\right)^3. \tag{10}$$

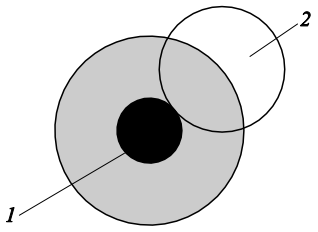


Figure 1. The excluded volume (shaded by gray) created by a resting particle (*1*) with respect to a moving particle (*2*).

Similarly, for the average particle volume and the average partial particle volume in a mixture one gets

$$\upsilon_0 \equiv \sum_i x_i \upsilon_{i0}, \qquad (11)$$

$$\upsilon^0 = \sum_i x_i \upsilon_i^0.$$

The exclusion factor f, the most important parameter of the theory, is defined as the ratio of the average excluded volume to the average particle volume in the system

$$f \equiv \frac{\upsilon^{\mathrm{ex}}}{\upsilon_0}. \qquad (12)$$

From Eqns (10) and (11) it follows that the exclusion factor f_0 for a rarefied gaseous mixture can be calculated using the relationship

$$f_0 = \frac{\upsilon^{\mathrm{ex}}}{\upsilon_0} = \frac{\sum_{i,k} x_i x_k \left(\upsilon_{i0}^{1/3} + \upsilon_{k0}^{1/3}\right)^3}{\sum_i x_i \upsilon_{i0}}. \qquad (13)$$

From here for a one-component system we again get $f_0 = 8$ (for mixtures, the f_0 value can be much smaller, remaining, however, greater than two).

Passage from rarefied to the condensed state is accompanied by clustering of matter, which causes a decrease in the exclusion factor.[38, 39, 42] The minimum value, $f = 1$, is only possible for 'soft' particles capable of filling the space without cavities; for hard particles the exclusion factor is always larger than unity and depends on the packing type. Generally, the excluded volume factor varies within the limits

$$f_0 \geqslant f \geqslant \frac{\upsilon_\infty}{\upsilon_0}, \qquad (14)$$

where υ_∞ is the limiting volume per particle. Equality of υ_∞ and υ_0 is only possible for 'soft' particles; otherwise, usually one has $\upsilon_\infty > \upsilon_0$. For instance, one gets $\upsilon_\infty/\upsilon_0 = 6/\pi \approx 1.91$ for a cubic packing of hard spheres and $\upsilon_\infty/\upsilon_0 = 6/\pi\sqrt{2} \approx 1.35$ for hexagonal packing. In any case the excluded volume factor varies in some narrow region within the interval $8 \geqslant f \geqslant 1$, whereas the pressure varies in a nearly unbounded interval. This makes the excluded volume factor a convenient tool in deriving the equation of state.

The formulation of theory begins with derivation of the master equation, that is, a rigorous thermodynamic relation to generate equations of state. We start from the Gibbs–Duhem equation

$$\mathrm{d}p = -s\mathrm{d}T + \sum_i c_i \mathrm{d}\mu_i, \qquad (15)$$

where s is the entropy density and c_i is the concentration of the ith component. Integration of Eqn (15) is performed at constant temperature and chemical composition (this limitation is removed after integration), so the concentration, c_i, of each component can be expressed through the overall concentration of all components $c = \sum_i c_i$, which becomes the exclusive integration variable. Substitution of expression (5) into relation (15) with allowance for Eqn (8) gives

$$\frac{\mathrm{d}p}{\mathrm{d}c} = \frac{k_\mathrm{B}T}{1 - c\upsilon^0}, \qquad (16)$$

where υ^0 is the average partial volume of the particle at rest according to definition (11). As mentioned above, the behaviour of the quantity is complex owing to competition between the attractive and repulsive forces, which precludes integration of Eqn (16) in the general form. To get around this problem, we first integrate Eqn (16) in the absence of long-range interactions [in this case, according to definition (6), υ^0 is 'automatically' transformed into υ^{ex}] and then add the long-range contribution p_l to the final expression. This gives the master equation in the form

$$p = k_\mathrm{B}T \int_0^c \frac{\mathrm{d}c}{1 - c\upsilon\mathrm{ex}} + p_\mathrm{l}. \qquad (17)$$

Expressions for p_l can be found in the literature. In particular, for the van der Waals forces one has

$$p_\mathrm{l} = -\sum_{i,k} \alpha_{ik} c_i c_k, \qquad (18)$$

where α_{ik} is the constant of attraction between particles of components i and k.

For simplicity, the master Eqn (17) can be written in a dimensionless form

$$\tilde{p} = \int_0^\varphi \frac{\mathrm{d}\varphi}{1 - f\varphi} + \tilde{p}_\mathrm{l}, \qquad (19)$$

where $\tilde{p} \equiv p\upsilon_0/k_\mathrm{B}T$ and $\tilde{p}_\mathrm{l}$ are respectively the dimensionless pressure and its long-range part and φ is the total volume fraction of all components as the sum of individual volume fractions φ_i

$$\varphi \equiv c\upsilon_0 = \sum_i c_i \upsilon_{i0} = \sum_i \varphi_i.$$

Correspondingly, Eqn (18) is transformed into

$$\tilde{p}_\mathrm{l} = -\sum_{i,k} \tilde{\alpha}_{ik} \varphi_i \varphi_k, \qquad (20)$$

where $\tilde{\alpha}_{ik} \equiv \alpha_{ik}\upsilon_0/k_\mathrm{B}T\upsilon_{i0}\upsilon_{k0}$ is the dimensionless image of the constant α_{ik}. In modern literature, the reduced density

$$y \equiv \frac{\sigma^3}{\upsilon} = \frac{6}{\pi}\varphi,$$

rather than the volume fraction φ (here, σ is the particle diameter) is often used. Clearly, this value corresponds to cubic packing of spheres, which, however, is not the closest packing. Having defined the reduced density in a more general form as follows

$$y \equiv \frac{\upsilon_\infty}{\upsilon},$$

(where υ_∞ can also belong to hexagonal packing), one gets an alternative dimensionless form of the master equation

$$\tilde{p}' = \int_0^y \frac{\mathrm{d}y}{1 - gy} + \tilde{p}_\mathrm{l}'. \qquad (21)$$

Here

$$\tilde{p}' \equiv \frac{p\upsilon_\infty}{k_\mathrm{B}T},$$

$g \equiv \upsilon^{\mathrm{ex}}/\upsilon_\infty$ is yet another exclusion factor. Correspondingly, the second dimensionless form of Eqn (18) is as follows:

$$\tilde{p}_\mathrm{l}' = -\sum_{i,k} \tilde{\alpha}'_{ik} y_i y_k, \qquad (22)$$

where $\tilde{\alpha}'_{ik}$ is the dimensionless attraction constant

$$\tilde{\alpha}'_{ik} \equiv \frac{\alpha_{ik}\upsilon_\infty}{k_\mathrm{B}T\upsilon_{i\infty}\upsilon_{k\infty}}.$$

For the most dense state the exclusion factor g equals unity; therefore, it is convenient to use Eqn (21) for the condensed state. But if one starts from the gaseous state, it's better to work with Eqn (19).

To calculate the integral in Eqn (19), one must know the function $f(\varphi)$. Information on this function for one-component systems can be extracted from virial coefficients. If we express the exclusion factor in terms of virial expansion [37, 38] and restrict to the ten known virial coefficients for the system of hard spheres,[55] the dependence of f on φ is characterised by a decreasing concave

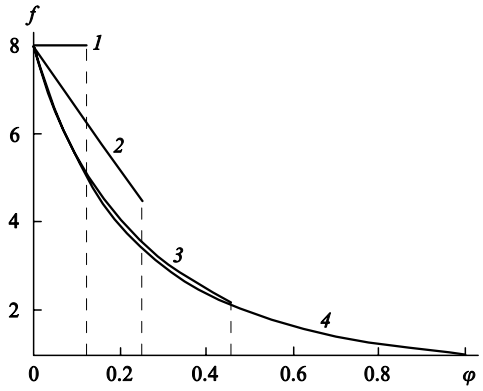


Figure 2. Exclusion factor plotted *vs.* volume fraction (solid lines) and the limits of applicability for the corresponding equations of state (dashed lines) with allowance for the short-range part only.
Planck equation (*1*), van der Waals equation (*2*), Eqn (38) (*3*) and the line obtained from the virial expansion for hard spheres with ten known virial coefficients (*4*).

curve (curve *4*, Fig. 2). The general form of the function $f(\varphi)$ is still unknown. However, taking into account that the exclusion factor can vary within narrow limits, one can hope for derivation of rather accurate equations of state using realistic approximations for the function $f(\varphi)$.

The simplest (zeroth) approximation is to use a constant exclusion factor f. Here, the equation of state is immediately derived from Eqn (19)

$$\tilde{p} = -\frac{\ln(1-f\varphi)}{f} + \tilde{p}_1 . \tag{23}$$

Particular cases of this equation are well known.

For a non-ionised monatomic gas with $f = 8$ and allowance for Eqn (20) one has

$$\tilde{p} = -\frac{\ln(1-8\varphi)}{8} - \tilde{\alpha}\varphi^2 . \tag{24}$$

This is neither more nor less than the Planck equation (2) written in a dimensionless form.

For the condensed state, taking into account Eqn (21) with $g = 1$ and Eqn (22), we get

$$\tilde{p}' = -\ln(1-y) - \tilde{\alpha}' y^2 . \tag{25}$$

This type of equation of state was derived by Temperley [56, 57] who applied the Ising model to the lattice gas condensation theory. Later, it was often used in lattice models.[58]

The next (first) approximation takes into account that the exclusion factor must decrease with an increase in density (a linear dependence is assumed)

$$f = f_0 - k\varphi . \tag{26}$$

Here, f_0 is the exclusion factor for rarefied gas and k is the a positive coefficient whose magnitude imposes limitations on the range of changes in φ. Substituting Eqn (26) into Eqn (19) gives the lattice gas equation of state in the first approximation

$$\tilde{p} = \int_0^{\varphi} \frac{\mathrm{d}\varphi}{1 - f_0\varphi + k\varphi^2} + \tilde{p}_1 . \tag{27}$$

The form of the function resulting from the integration depends on the numerical value of the constant k; therefore, expression (27) in fact defines a family (namely, three types [37–39, 41]) of equations of state rather than a single equation of state. When using this approximation and higher approximations, we are guided by the principle of maximum simplicity of the solution. In this case, we take $k = (f_0/2)^2$ and the equation of state has the form:

$$\tilde{p} = \frac{\varphi}{1 - (f_0/2)\varphi} + \tilde{p}_1 . \tag{28}$$

With allowance for Eqn (20) and $f_0 = 8$, Eqn (28) for a one-component system with van der Waals forces takes the form

$$\tilde{p} = \frac{\varphi}{1 - 4\varphi} - \tilde{\alpha}\varphi^2 . \tag{29}$$

This is neither more nor less than the van der Waals equation (1) written in a dimensionless form.

Now we can clearly see the sense of the coefficient 4 in Eqn (1) and resolve the apparent contradiction between the van der Waals and Planck equations. Namely, the factor $4v_0$ in the van der Waals equation is not the excluded volume. This equation does not include a constant excluded volume at all; rather, the excluded volume in this equation is variable. The van der Waals equation ranks higher than the Planck equation in the hierarchy of approximations, though the place occupied by the former is not the place of honour.

In the second approximation [37–43] we model the concavity of the $f(\varphi)$ curve using a fractional-linear function

$$f = \frac{f_0 - k_1\varphi}{1 + k_2\varphi} \tag{30}$$

with two positive constants k_1 and k_2. Yet another positive constant K is introduced to characterise the initial (negative) slope of the curve $f(\varphi)$

$$\left(\frac{\mathrm{d}f}{\mathrm{d}\varphi}\right)_{\varphi \to 0} = -K . \tag{31}$$

To calculate K, it is sufficient to know the second and third virial coefficients. For a one-component system, one has $K = 34$. From Eqns (30) and (31) one gets the relation

$$k_1 + k_2 f_0 = K \tag{32}$$

connecting the coefficient k_1 to k_2; as a result, only one of them can be chosen independently.

Substituting Eqn (30) into the master equation (19) leads to

$$\tilde{p} = \int_0^{\varphi} \frac{(1 - k_2\varphi)\mathrm{d}\varphi}{1 - (f_0 - k_2)\varphi + k_1\varphi^2} + \tilde{p}_1 , \tag{33}$$

and its simplest form after integration meets the condition

$$k_1^{1/2} = \frac{f_0 - k_2}{2} \equiv \beta . \tag{34}$$

Taken together, this relationship and Eqn (32) unambiguously determine the coefficients k_1 and k_2

$$k_1 = (f_0 - K^{1/2})^2 , \tag{35}$$

$$k_2 = 2K^{1/2} - f_0 .$$

With k_1 and k_2 thus determined, the equation of state in the second approximation has the form

$$\tilde{p} = \frac{f_0 - \beta}{\beta}\frac{\varphi}{1 - \beta\varphi} + \frac{f_0 - 2\beta}{\beta^2}\ln(1 - \beta\varphi) + \tilde{p}_1 , \tag{36}$$

where

$$\beta = f_0 - K^{1/2} .$$

Using Eqn (20), Eqn (36) for a nonionic system with van der Waals forces can be written in a more detailed form

$$\tilde{p} = \frac{f_0 - \beta}{\beta}\frac{\varphi}{1 - \beta\varphi} + \frac{f_0 - 2\beta}{\beta^2}\ln(1 - \beta\varphi) - \sum_{i,k}\tilde{\alpha}_{ik}\varphi_i\varphi_k . \tag{37}$$

For a one-component system, one has $f_0 = 8$, $K = 34$ and $\beta \approx 2.169$. In this case Eqn (37) takes the form

$$\tilde{p} = \frac{2.688\varphi}{1 - 2.169\varphi} + 0.778\ln(1 - 2.169\varphi) - \tilde{\alpha}\varphi^2. \tag{38}$$

Equation (38) looks like a combination of the van der Waals and Planck equations, being much more accurate than both of them and provides exact values of the first three rather than two virial coefficients. This equation describes a gas–liquid phase transition and the critical point. A comparison of the critical parameters of the three equations [37–39, 41] revealed their improvement on going up in the hierarchy of approximations. One of the critical parameters of Eqn (38) can be treated outstandingly, *viz*., the ratio of the Boyle temperature (T_B) to the critical temperature (T_c) is 2.74 (*cf*. a value of 2.75 determined from experiments).

Figure 2 shows how the range of applicability of the equation of state extends in the hierarchy of approximations. Indeed, one has $\varphi < 0.125$ for the Planck equation, $\varphi < 0.25$ for the van der Waals equation and $\varphi < 0.461$ for Eqn (38); but this is much smaller than $\varphi = 0.74$ for the closest packing of hard spheres. Therefore, all three equations are applicable to gases. Nevertheless, Eqn (36) can be adapted to the whole density range. The case in point is that this equation gives the correct value of the second virial coefficient irrespective of the parameter β, which thus is responsible for the correctness of the value of the third virial coefficient. Losing quality of the equation, it is possible to use a fitting parameter k instead of β and write the equation of state for a system of hard spheres of the same size as

$$\tilde{p} = \frac{8 - k}{k}\frac{\varphi}{1 - k\varphi} + \frac{8 - 2k}{k^2}\ln(1 - k\varphi), \tag{39}$$

and then determine the k value assuming the best correspondence between Eqn (39) and the results of a molecular dynamics simulation.[6] This procedure can be illustrated by Fig. 3; the k and cross-correlation square R^2 (this parameter characterises the quality of computer fitting) values are listed in Table 1. As can be seen, while the curve plotted using Eqn (39) passes near the 'experimental' points, the amplitude of deviations (1% – 10%) is too large to meet modern requirements.

The third and higher approximations were derived by successively adding the terms next in order of smallness to the numerator of expression (30) while the principle of maximum simplicity was realised by choosing the coefficients reducing the denominator of the first term of the equation of state to an integer power of the difference. All coefficients were expressed through the same

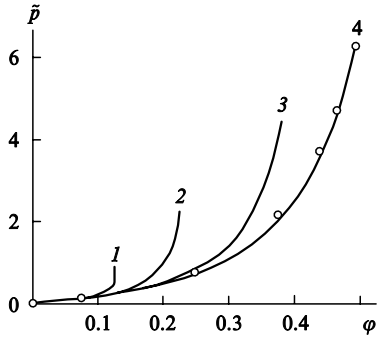


Figure 3. Dimensionless pressure isotherms for a fluid of hard spheres obtained in the zeroth (Planck equation, curve *1*), first (van der Waals equation, curve *2*) and second [Eqn (38), curve *3*] approximations of the equation of state for a gas derived in the framework of the theory of excluded volume and using Eqn (39) (curve *4*) for the entire density range. Points denote the results of molecular dynamics simulations reported by Alder and Wainwright.[6]

Table 1. Coefficient k and cross-correlation square R^2 obtained in different approximations of the equation of state for the whole range of densities in fitting the Alder and Wainwright [6] and Erpenbeck and Wood [59] databases.

Approximation number	Database [6]		Database [59]	
	k	R^2	k	R^2
2	1.592960	0.994418	1.597202	0.989454
3	1.283681	0.997342	1.299441	0.998856
4	1.070709	0.999457	1.077599	0.999684
5	0.918766	0.999847	0.921284	0.999920
6	0.805259	0.999945	0.805372	0.999988
6′	0.803025	0.999952	0.802941	0.999994
7	0.717260	0.999946	0.715955	0.999998
8	0.563023	0.998591	0.608111	0.999611

constant k. The third and higher approximations contain no logarithms and can be expressed using a general relationship

$$\tilde{p}^{(n)} = \frac{1}{(1 - k\varphi)^{n-1}}\left\{\varphi + \frac{f_0 - 2k(n-1)}{(n-1)(n-2)k^2} \times \right. \tag{40}$$
$$\left. \times \left[(1 - k\varphi)^{n-1} - 1 + (n-1)k\varphi\right]\right\} + \tilde{p}_1,$$

where n is the approximation number ($n \geqslant 3$). It is acceptable to write the equation of state in terms of a compressibility factor (especially for the model of hard spheres)

$$Z \equiv \frac{pv}{k_B T} = \frac{\tilde{p}}{\varphi}. \tag{41}$$

Using this technique, we rewrite relationship (40) for a fluid of hard spheres of the same size ($f_0 = 8$, $\tilde{p}_1 = 0$) in the form

$$Z^{(n)} = \frac{1}{(1 - k\varphi)^{n-1}}\left\{1 + \frac{8 - 2k(n-1)}{(n-1)(n-2)k^2\varphi} \times \right. \tag{42}$$
$$\left. \times \left[(1 - k\varphi)^{n-1} - 1 + (n-1)k\varphi\right]\right\}.$$

In this category the Carnahan–Starling equation [60]

$$Z = \frac{1 + \varphi + \varphi^2 - \varphi^3}{(1 - \varphi)^3}, \tag{43}$$

obtained by summing the virial expansion with coefficients rounded to integers is thought to be the most accurate. Before this equation (at first, in the framework of scaled particle theory [4]), the Percus–Yewick equation [61, 62]

$$Z = \frac{1 + \varphi + \varphi^2}{(1 - \varphi)^3}, \tag{44}$$

$$Z = \frac{1 + 2\varphi + 3\varphi^2}{(1 - \varphi)^2}, \tag{45}$$

(in the form of the compressibility and pressure equations, respectively) and the Guggenheim equation [63]

$$Z = \frac{1}{(1 - \varphi)^4}. \tag{46}$$

were derived. Here, we don't present well-established, more complex equations of state (Padé approximants,[64] Le Fevre equation,[65] Woodcock equation,[66] *etc*.) because they are not related to the approach in question and are inconsistent with the concept of maximum simplicity.

Returning to Eqn (42), we will make some comments concerning particular approximations. For the third, fourth and fifth approximations we get the following equations of state:

$$Z^{(3)} = \frac{1 + (4 - 2k)\varphi}{(1 - k\varphi)^2}, \tag{47}$$

$$Z^{(4)} = \frac{1 + (4 - 3k)\varphi + k(k - 4/3)\varphi^2}{(1 - k\varphi)^3}, \tag{48}$$

$$Z^{(5)} = \frac{1 + (2/3)(1 - k)(6\varphi - 4k\varphi^2 + k^2\varphi^3)}{(1 - k\varphi)^4}. \tag{49}$$

With $k = 1$, Eqn (47) is a truncated Percus – Yewick equation (45), relationship (48) is similar to the Carnahan – Starling equation (43) and the Percus – Yewick equation (44), while equation (49) coincides with the Guggenheim equation (46).

The reader can assure himself that Eqn (42) gives the correct value of the second virial coefficient irrespective of the value of k. In other words, Eqn (42) can be applied to a gas of hard spheres at any value of the constant k that can be used as a parameter of fitting to the results of numerical experiments for all densities; this is the best way to refine Eqn (42). This was done [67, 68] using the first database by Alder and Wainwright [6] (see above) and the highly accurate but covering the range of lower densities database by Erpenbeck and Wood [59]. Table 1 lists the k values thus found for each approximation and the cross-correlation squares R^2. As can be seen, the highest accuracy of equation (42) is achieved in the seventh approximation. Passage to higher approximations is pointless because starting from the eighth approximation the results of fitting become much poorer owing to the use of only one parameter. It should be noted that already in the third approximation the region of formally admissible changes in the volume fraction, $0 \leqslant \varphi \leqslant 0.779$, is broader than the region of formally admissible changes for a system of hard spheres, $0 \leqslant \varphi \leqslant 0.74$, which ensures coverage of all possible densities.

The sixth approximation of Eqn (42) deserves particular attention With the k value listed in Table 1, which nearly coincides for both databases, this approximation has the numerical form

$$Z^{(6)} = \frac{1 - 0.026(\varphi - 0.805\varphi^2 + 0.324\varphi^3 - 0.052\varphi^4)}{(1 - k\varphi)^5}. \tag{50}$$

The smallness of the coefficient 0.026 allows the numerator to be truncated to unity. Having done this, one gets an approximation (denoted by 6′)

$$Z^{(6')} = (1 - k\varphi)^{-5}, \tag{51}$$

which combines a very simple form with high accuracy. Indeed, after repeating the fitting procedure using Eqn (51) and getting somewhat different k values (see Table 1) we find that Eqn (51) is the most accurate among all approximations (with a maximum deviation of less than 1%) evaluated using the Alder and Wainwright database. A comparison of the accuracy of Eqn (51) with the accuracy of the Carnahan – Starling equation (43) and other equations of state (even complex equations including the most accurate Woodcock equation [66]) shows the advantage of Eqn (51).[45, 46] Evaluated with the highly accurate Erpenbeck and Wood database, Eqn (51) occupies an intermediate position between the sixth and seventh approximations, being characterised by a maximum deviation of 0.45%. Here, the Carnahan – Starling equation provides a maximum deviation of 0.31% while Eqn (42) in the seventh approximation is characterised by a deviation of only 0.20% (see Ref. 68) (the Woodcock equation was evaluated using another database and was characterised by a deviation of 0.59%).

Thus, at present Eqn (42) at $n = 7$ is one of the most accurate equations of state (maybe, the most accurate one). It should be noted that in comparing the equations of state a question of the accuracy of the database is posed.[6] As it is improved, the procedure can be repeated for any other set of reference data, which allows the coefficient k in Eqns (42) and (40) to be refined.

III. Equation of state for surface monolayers

A technique similar to that considered above was applied to the analysis of a surface monolayer formed on adsorption or spreading of a substance on the surface. The surface area was considered instead of volume. However, it is incorrect to reason that transition from the equation of state for bulk systems to the equation of state for a monolayer is reduced to trivial reduction of the equation dimension. The volume, v_0, of anisometric particles is independent while their parking area, a_0, depends on the spatial orientation, which complicates the computational procedure. The necessity of taking into account the effect of the substrate also goes beyond the two-dimensional approach. Thus, strictly speaking, description of a monolayer requires a three-dimensional theory based on the same expression (5) for the chemical potential of matter in the bulk system.

Consider a multicomponent monolayer on a planar (solid or liquid) substrate. Since only the surface characteristics are important for the equation of state, the monolayer will be thought insoluble; this will permit a rigorous treatment in terms of equilibrium thermodynamics. The main relationship in this theory is the Gibbs adsorption equation

$$\mathrm{d}\gamma = -\bar{s}\mathrm{d}T - \sum_i \Gamma_i \mathrm{d}\mu_i, \tag{52}$$

where γ is the surface tension, $\bar{s}$ is the entropy excess per unit surface area and Γ_i and μ_i are the adsorption (excess of substance per unit surface area) and the chemical potential of particles (molecules, ions or nanoparticles) of component i in the monolayer. Summation is performed over all components of the monolayer but does not involve the substrate whose influence is included in all other parameters. For insoluble monolayers the adsorption Γ_i coincides with the actual amount of matter per unit surface area of the monolayer. In other words, Γ_i is the surface concentration of particles of the sort i, related to conventional (three-dimensional) concentration as follows

$$c_i = \frac{\Gamma_i}{h_i}, \tag{53}$$

where h_i is the average size of particles of the sort i in the direction perpendicular to the plane of the monolayer. Clearly, if we deal with aspherical particles, the parameter h_i is sensitive to their orientation.

According to the Gibbs equation of adsorption, the presence of a substrate causes a decrease in the surface tension of the monolayer. The difference

$$\Pi_0 \equiv \gamma_0 - \gamma, \tag{54}$$

(γ_0 is the surface tension of the substrate in the absence of a monolayer) is called the surface pressure; this is the main characteristic of the monolayer. Substituting Eqn (54) into Eqn (52) gives the equation

$$\mathrm{d}\Pi = \bar{s}\mathrm{d}T + \sum_i \Gamma_i \mathrm{d}\mu_i, \tag{55}$$

which is similar to the Gibbs – Duhem equation (15). Equations (5), (53) and (55) serve as the basis of a theory which also operates with some geometric characteristics considered below.

The most important geometric characteristics of the particles of component i in the monolayer are the parking area a_{i0}, the minimum possible surface area per particle $a_{i\infty}$ at $\Pi \to \infty$, the partial surface area a_i, the partial surface area of a particle at rest a_i^0 and the excluded surface area a_i^{ex} defined as the partial area of a particle at rest in the absence of long-range forces [47 – 49]

$$a_i^{\mathrm{ex}} \equiv a_i^0 \equiv \left(\frac{\partial A}{\partial N_i^0}\right)_{T, \Pi, N_j, N_{j\neq 1}^{\mathrm{o}}}, \tag{56}$$

where A is the surface area of the monolayer. The partial surface areas obey the following relations

$$a_i = \left(\frac{\partial \mu_i}{\partial \Pi}\right)_{T,\{x\}}, \qquad (57)$$

$$a_i^0 = \left(\frac{\partial \mu_i^0}{\partial \Pi}\right)_{T,\{x\}},$$

where $\{x_i\}$ is the set of mole fractions of the components

$$x_i \equiv \frac{\Gamma_i}{\Gamma}, \qquad (58)$$

$$\Gamma \equiv \sum_i \Gamma .$$

Out of two relations (57) the latter was derived recently.[47]

The multicomponent monolayer is also characterised by the average geometric parameters:

$$a_0 \equiv \sum_i x_i a_{i0}, \qquad (59)$$

$$a_\infty \equiv \sum_i x_i a_{i\infty}, \qquad (60)$$

$$a \equiv \sum_i x_i a_i, \qquad (61)$$

$$a^0 \equiv \sum_i x_i a_i^0, \qquad (62)$$

$$a^{ex} \equiv \sum_i x_i a_i^{ex}, \qquad (63)$$

$$h \equiv \sum_i x_i h_i . \qquad (64)$$

The parameter h can be treated as the average monolayer thickness.

Integration of Eqn (55) assuming constant temperature and composition taking into account Eqns (5), (53) and (56)–(64) gives the master equation

$$\Pi = k_B T \int_0^\Gamma \frac{1 - c\mathrm{d}h/\mathrm{d}\Gamma}{1 - \Gamma a^{ex}} \mathrm{d}\Gamma + \Pi_1, \qquad (65)$$

where Π_1 is the long-range part of the surface pressure. For instance, in the case of the van der Waals interaction one has

$$\Pi_1 = -\sum_{i,k} \alpha_{ik} \Gamma_i \Gamma_k . \qquad (66)$$

Equation (65) is an analogue of the master Eqn (17) for bulk phases but has a more complex form owing to the orientation effect ($\mathrm{d}h/\mathrm{d}\Gamma$ derivative). At a specified particle orientation or in the case of spherical particles, the derivative $\mathrm{d}h/\mathrm{d}\Gamma$ vanishes and the master equation takes the two-dimensional form

$$\Pi = k_B T \int_0^\Gamma \frac{\mathrm{d}\Gamma}{1 - \Gamma a^{ex}} + \Pi_1, \qquad (67)$$

suitable for the derivation of two-dimensional equations of state.

Using a_0 or a_∞, Eqn (67) can be written in a dimensionless form in two alternative ways. The first form is

$$\tilde{\Pi} = \int_0^\varphi \frac{\mathrm{d}\varphi}{1 - f\varphi} + \tilde{\Pi}_1, \qquad (68)$$

where $\tilde{\Pi} \equiv \Pi a_0 / k_B T$ and $\tilde{\Pi}_1$ are respectively the dimensionless surface pressure and its long-range part, $\varphi \equiv \Gamma a_0$ is the total surface fraction of components of the monolayer and $f \equiv a^{ex}/a_0$ is the exclusion factor. The second form is as follows

$$\tilde{\Pi}' = \int_0^\theta \frac{\mathrm{d}\theta}{1 - g\theta} + \tilde{\Pi}_1', \qquad (69)$$

where the dimensionless surface pressure is given by $\tilde{\Pi}' \equiv \Pi a_\infty / k_B T$, $\theta \equiv \Gamma a_\infty$ is the surface coverage degree and g is the second exclusion factor

$$g \equiv \frac{a^{ex}}{a_\infty} = \frac{f a_0}{a_\infty}. \qquad (70)$$

In the case of van der Waals interactions the long-range part of the surface pressure in Eqns (68) and (69) has the form

$$\tilde{\Pi}_1 = -\sum_{i,k} \tilde{\alpha}_{ik} \varphi_i \varphi_k , \qquad (71)$$

$$\tilde{\Pi}_1' = -\sum_{i,k} \tilde{\alpha}_{ik}' \theta_i \theta_k , \qquad (72)$$

where $\tilde{\alpha}_{ik} \equiv \alpha_{ik} a_0 / k_B T a_{i0} a_{k0}$ and $\tilde{\alpha}_{ik}' \equiv \alpha_{ik} a_\infty / k_B T a_{i\infty} a_{k\infty}$. Of course, Eqns (68) and (69) are equivalent and the use of a particular equation is governed by convenience. Equation (68) is more appropriate for the gaseous state while Eqn (69) is better for the condensed state.

The functions $f(\varphi)$ and $g(y)$ in Eqns (68) and (69) are still unknown, but the ranges of their changes are available.[48, 52–54] For a gas, the average exclusion factor in the multicomponent monolayer can be calculated with ease using the relationship

$$f_0 = \frac{\sum_{i,k} x_i x_k \left(a_{i0}^{1/2} + a_{k0}^{1/2}\right)^2}{\sum_i x_i a_{i0}}. \qquad (73)$$

Equation (73) gives $f_0 = 4$ for one-component and even smaller f_0 for multicomponent monolayers. This is the maximum value of the exclusion factor in the absence of clustering. Analysis of two-dimensional clustering[48, 52–54] defines the minimum value of the exclusion factor as $f_\infty = a_\infty / a_0$ (packing type dependent parameter). Then, in accord with Eqn (70), the minimum value of g must be $g_\infty = 1$. In any case the exclusion factor varies within the interval $4 > f$, $g > 1$, which is narrower than for three-dimensional systems. Correspondingly, one can also expect a higher accuracy of the equation of state when using approximations for the functions $f(\varphi)$ and $g(y)$.

Consider two-dimensional equations of state that follow from Eqns (68) and (69). In the zeroth approximation the exclusion factor is thought to be constant, which is possible only for a narrow interval of gas or fluid states. In this case, Eqns (68) and (69) take the form

$$\tilde{\Pi} = -\frac{\ln(1 - f\varphi)}{f} + \tilde{\Pi}_1, \qquad (74)$$

$$\tilde{\Pi}' = -\frac{\ln(1 - g\theta)}{g} + \tilde{\Pi}_1'. \qquad (75)$$

Equation (74) for a rarefied non-ionised gas with $f = f_0 = 4$ and allowance for expression (71) is transformed to

$$\tilde{\Pi} = -\frac{\ln(1 - 4\varphi)}{4} - \tilde{\alpha}\varphi^2. \qquad (76)$$

This is a two-dimensional analogue of the Planck equation (24), which also gives the exact value of the second virial coefficient of two-dimensional virial expansion. By replacing the factor 4 in Eqn (76) by f_0 in accord with Eqn (73) we get a general expression for a two-dimensional gaseous mixture.

Equation (75) with $g = 1$ gives two famous equations. At $\tilde{\Pi}_1' = 0$, it represents the van Laar equation of state for an ideal monolayer

$$\tilde{\Pi}' = -\ln(1 - \theta), \qquad (77)$$

whose form is independent of the number of components.[27] If (again with $g = 1$) the parameter $\tilde{\Pi}'_1$ is expressed in the form (72), Eqn (75) represents the generalised Frumkin equation [28,29] written in a dimensionless form

$$\tilde{\Pi}' = -\ln(1-\theta) - \sum_{i,k} \tilde{\alpha}'_{ik}\theta_i\theta_k\,. \tag{78}$$

For one-component systems the equation of state (78) takes the form

$$\tilde{\Pi}' = -\ln(1-\theta) - \tilde{\alpha}'\theta^2. \tag{79}$$

It corresponds to the Frumkin equation (4) written in a dimensionless form, which is transformed into the van Laar equation at $\tilde{\alpha}' = 0$.

Starting from the gaseous state, we must assume that the exclusion factor decreases as the surface density increases. To a first approximation, the exclusion factor f is a linear function of φ

$$f = f_0 - k_1\varphi, \tag{80}$$

where k_1 is a positive constant. Substituting the dependence (80) into Eqn (68) gives a family of equations of state. The simplest of them meets the condition $k_1 = f_0^2/4$ and has the form

$$\tilde{\Pi} = \frac{\varphi}{1-(f_0/2)\varphi} + \tilde{\Pi}_1\,. \tag{81}$$

Substituting expression (71) into Eqn (81), we get the generalised van der Waals equation written in a dimensionless form

$$\tilde{\Pi} = \frac{\varphi}{1-(f_0/2)\varphi} - \sum_{i,k} \tilde{\alpha}_{ik}\varphi_i\varphi_k\,. \tag{82}$$

For a one-component system ($f_0 = 4$) Eqn (82) takes the dimensionless form of the two-dimensional van der Waals equation (3)

$$\tilde{\Pi} = \frac{\varphi}{1-2\varphi} - \tilde{\alpha}\varphi^2. \tag{83}$$

In the second approximation, a new equation of state is derived.[47,48,51,52] The procedure is the same as that employed in the case of three dimensions [see Eqns (30)–(36)]. Starting from condition (30), we get the two-dimensional equation of state

$$\tilde{\Pi} = \frac{f_0-\beta}{\beta}\frac{\varphi}{1-\beta\varphi} + \frac{f_0-2\beta}{\beta^2}\ln(1-\beta\varphi) + \tilde{\Pi}_1\,, \tag{84}$$

where again $\beta = f_0 - K^{1/2}$. Equations (84) and (36) have the same form, but all coefficients are different. In the case of van der Waals forces, substitution of Eqn (71) provides a more detailed equation of state

$$\tilde{\Pi} = \frac{f_0-\beta}{\beta}\frac{\varphi}{1-\beta\varphi} + \frac{f_0-2\beta}{\beta^2}\ln(1-\beta\varphi) - \sum_{i,k} \tilde{\alpha}_{ik}\varphi_i\varphi_k\,. \tag{85}$$

A one-component monolayer is characterised [47,48,51,52] by $f_0 = 4$, $K = 6.616$ and $\beta = 1.428$. Substituting these values into Eqn (85) leads to

$$\tilde{\Pi} = \frac{1.801\varphi}{1-1.428\varphi} + 0.561\ln(1-1.428\varphi) - \tilde{\alpha}\varphi^2. \tag{86}$$

This is a two-dimensional equation of state in the second approximation. Unfortunately, the two-dimensional gaseous state has been studied much less than the three-dimensional state. Equation (86) can be evaluated in two ways, by comparison with the van der Waals equation (83) and by comparing the values of the virial coefficients.[16,69] The applicability range of Eqn (86) ($0 < \theta < 0.7$) is much broader compared to the van der Waals equation ($0 < \theta < 0.5$), the former being much more accurate. If the van der Waals equation gives exact values of the first and the second virial coefficients only, Eqn (86) exactly reproduces the first, second and third virial coefficients and provides a nearly exact value of the fourth virial coefficient (overestimated by 9%) and the fifth virial coefficient overestimated by 28%.

It is of interest to compare Eqns (38) and (86). As was expected, the two-dimensional equation is more accurate. Until recently, only the van der Waals equation simultaneously covered the three-dimensional and two-dimensional cases. Making use of the situation, de Boer showed [26] that for the same substance the two-dimensional critical temperature $T_c^{(2)}$ must be half the three-dimensional critical temperature $T_c^{(3)}$. Evaluation [49] using Eqns (38) and (86) revealed that

$$\frac{T_c^{(2)}}{T_c^{(3)}} \approx 0.455. \tag{87}$$

The raito (87) shows that the de Boer estimate $T_c^{(2)}/T_c^{(3)} \approx 0.5$ is quite correct, being at the same time somewhat rough.

Higher approximations are derived using the same algorithm as for the bulk phases. A general formula for the nth approximation ($n \geqslant 3$) is as follows

$$\tilde{\Pi}^{(n)} = \frac{\varphi}{(1-k\varphi)^{n-1}}\left\{1 - \frac{2nk-2k-f_0}{(n-1)(n-2)k^2\varphi} \times \left[(1-k\varphi)^{n-1} - 1 + (n-1)k\varphi\right]\right\} + \tilde{\Pi}_1\,. \tag{88}$$

It is easy to verify that Eqn (88) gives correct values of the first and second virial coefficients irrespective of the choice of the constant k. This assures applicability of Eqn (88) to the gaseous state of the monolayer at any k value and allows k to be used as a fitting parameter for the whole density range. Here, it is convenient to use an ultrahigh-precision (to 0.01%) data array obtained by Monte Carlo simulation and molecular dynamics.[30] Let us demonstrate the procedure taking a model of hard disks as an example.

Let the disks be of the same size, $\tilde{\Pi}_1 = 0$ and $f_0 = 4$. Rewrite Eqn (88) using the compressibility factor $Z = \tilde{\Pi}/\varphi$,

$$Z^{(n)} = \frac{1}{(1-k\varphi)^{n-1}}\left\{1 - \frac{2nk-2k-4}{(n-1)(n-2)k^2\varphi} \times \left[(1-k\varphi)^{n-1} - 1 + (n-1)k\varphi\right]\right\}. \tag{89}$$

In accord with expression (89), the equation of state in the third approximation has the form

$$Z^{(3)} = \frac{1-2(k-1)\varphi}{(1-k\varphi)^2}\,. \tag{90}$$

With $k = 1$ Eqn (90) reproduces the equation of state known in scaled particle theory [70,71]

$$Z^{(3)} = (1-\varphi)^{-2}. \tag{91}$$

In addition, Eqn (91) is a two-dimensional analogue of the Carnahan–Starling equation (43) for hard spheres, *i.e.*, it is obtained by summing the two-dimensional virial expansion in which all coefficients are rounded to integers. Equation (91) is also similar to the Henderson equation [72]

$$Z = \frac{1+(b_3-3)\varphi^3}{(1-\varphi)^2} \tag{92}$$

with $b_3 - 3 \approx 0.128$. Equation (90) best fits the reference database [30] at $k \approx 1.0145$ (cross-correlation squared is 0.999908 with a maximum deviation of $\sim$1%) and the form of Eqn (90) is as follows

$$Z^{(3)} = \frac{1 - 0.029\varphi}{(1 - 1.0145\varphi)^2}. \quad (93)$$

Since the k values found do approach unity, expression (91) can be used as the equation of state in the third approximation. In this case a small decrease in accuracy (maximum deviation increases to 3%) is compensated for by the simplicity of the equation. Thus, we can say that scaled particle theory reproduces the third approximation to the theory of excluded area.

Going to the fourth approximation from Eqn (89) gets

$$Z^{(4)} = \frac{1 - (3k - 2)\varphi + k(k - 2/3)\varphi^2}{(1 - k\varphi)^3}. \quad (94)$$

Equation (94) best fits the database [30] at $k \approx 0.876677$ (cross-correlation squared is 0.99999 with a maximum deviation of $\sim 0.46\%$). With this k value Eqn (94) takes the form

$$Z^{(4)} \approx \frac{1 - 0.63\varphi + 0.184\varphi^2}{(1 - 0.876677\varphi)^3}. \quad (95)$$

The next (fifth) approximation gives somewhat poorer results (cross-correlation squared is 0.99993), which can be explained by the use of a sole fitting parameter.

Among the studies reported in the last decade, a simple equation of state [35, 36] based on the Boltzmann concept of excluded volume must be pointed out. In our notation, the equation has the form

$$Z = \left(1 - 2\varphi + \frac{2\varphi_\infty - 1}{\varphi_\infty^2}\varphi^2\right)^{-1} = \left[1 - 2\varphi_\infty\theta + (2\varphi_\infty - 1)\theta^2\right]^{-1}, \quad (96)$$

where $\varphi_\infty = a_0/a_\infty = 3^{1/2}\pi/6 \approx 0.9069$ is the upper limit for φ, which corresponds to the closest hexagonal packing, and $\theta = \varphi/\varphi_\infty$ is the surface coverage degree. The authors of the study [35] compared the accuracy of their equation with the available simple and complex equations including, except for expressions (91) and (92), the equations of state by Andrews,[73, 74] Woodcock,[66] Baram and Luban[75] and the Levin [30] and Padé [76] approximants. It was concluded that Eqn (96) is the most accurate among the simple equations. However, a comparative analysis [53] of Eqns (95) and (96) showed that expression (95) is even better, being the best among the simple equations; only the Levin approximant (the most accurate among the complex equations) ranks above it in accuracy.

IV. The orientation equation of state

Let us return to Eqn (65) and discuss the role of orientation characterised by the derivative $\mathrm{d}h/\mathrm{d}\Gamma$. To state that an increase in the surface density of a substance must lead to thickening of a monolayer as the main trend probably requires the mass balance only. But from Eqn (65) it is seen that if $\mathrm{d}h/\mathrm{d}\Gamma > 0$ and the derivative is rather large in absolute value, then, possibly, the perfect derivative $\mathrm{d}\Pi/\mathrm{d}\Gamma$ will be of negative sign, which means stability violation. As a result, a van der Waals loop corresponding to the first-order phase transition can appear in the two-dimensional pressure isotherm. Thus, the first important conclusion that follows from Eqn (65) is that orientation of the particles of the monolayer can induce two-dimensional first-order phase transitions. It is remarkable that this prediction is also valid in the absence of attractive forces between anisometric particles. The effect of orientation on two-dimensional condensation was demonstrated in the experiments with surfactant monolayers.[77]

To make Eqn (65) complete, one should know the dependence of the monolayer thickness h on the surface density Γ. In the general case the functional dependence

$$h = h(T, \Gamma_1, \Gamma_2, ...) \quad (97)$$

can be called the orientation equation of state. Neither theoretical nor experimental data on such an equation are available at the moment but the first steps towards formulation of a theory have been made recently.[47, 51–53] Of course, the cases in point are general considerations because the orientation effects strongly depend on the specific geometry of particles in the monolayer.

Apparently, the orientation effect arises in the gaseous monolayer. Since particles change their orientations by collisions, one can assume that the increase in the thickness, $h - h_0$, is proportional to the collision rate, which in turn is proportional to the square of the particle concentration and to the collision diameter that is determined by the linear dimension of the particles along the surface. If the parking area of particles is proportional to the square of the linear dimension mentioned above and its product by h (particle volume) is a constant, the linear dimension is proportional to the square root of the thickness. Then, one gets the orientation equation of state

$$h - h_0 = \frac{K\varphi^2}{h^{1/2}}, \quad (98)$$

where h_0 is the minimum thickness of the monolayer at zero surface pressure and K is the coefficient of proportionality. Analysis and refinement of Eqn (98) should be set aside until experimental data in the field is obtained.

A model of elastic behaviour can also be applied to a condensed monolayer. This approach was used in the membrane theory [78] by introducing a 'tilt modulus' which has not been determined experimentally so far. Using the variable θ, which is more convenient for description of the condensed state, expression (65) can be replaced by an equivalent equation

$$\tilde{\Pi}' = \int_0^\theta \frac{1 - \mathrm{d}\ln h/\mathrm{d}\ln\theta}{1 - g\theta}\mathrm{d}\theta + \tilde{\Pi}_1', \quad (99)$$

where $\tilde{\Pi}'$ and $\tilde{\Pi}_1'$ have the same sense as in expression (69). In particular, for a non-ionised monolayer one has

$$\tilde{\Pi}_1' = -\tilde{\alpha}'\theta^2,$$

where $\tilde{\alpha}' \equiv \alpha/k_\mathrm{B}Ta_\infty$ is the dimensionless attracting constant. It is reasonable to assume that the monolayer acquires elastic properties after exceeding a threshold degree of coverage θ_t. The action of tangential stress, Π/h, causes the monolayer to thicken. Let us introduce the transversal elasticity modulus

$$\varepsilon = \frac{\mathrm{d}(\Pi/h)}{\mathrm{d}\ln h}. \quad (100)$$

Integrating relationship (100) gives the equation of state

$$\Pi = \frac{\Pi_\mathrm{t}h}{h_\mathrm{t}} + \varepsilon h\ln\left(\frac{h}{h_\mathrm{t}}\right), \quad (101)$$

where the particular Π_t and h_t values correspond to θ_t, *i.e.*, to the transition to elastic orientation. Such a transition usually manifests itself as a kink point in the surface pressure isotherm (Fig. 4), so the Π_t can be readily determined in the experiment. In addition to the minimum thickness h_0 it is also convenient to introduce the maximum thickness h_∞ corresponding to the closest packing of the monolayer at an infinite pressure. Then, Eqn (101) can be written in a dimensionless form

$$\Pi' = \frac{\tilde{\Pi}_\mathrm{t}'\tilde{h}}{\tilde{h}_\mathrm{t}} + \tilde{\varepsilon}\tilde{h}\ln\left(\frac{\tilde{h}}{\tilde{h}_\mathrm{t}}\right), \quad (102)$$

where $\tilde{\varepsilon} \equiv \varepsilon a_\infty h_\infty/k_\mathrm{B}T$ and $\tilde{h} \equiv h/h_\infty \leqslant 1$ are the reduced elastic modulus and monolayer thickness, respectively.

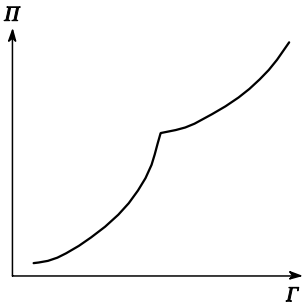


Figure 4. Surface pressure isotherm for the case of an orientation two-dimensional second-order phase transition.

For a dense monolayer we can assume $a^{ex} = a$ and correspondingly

$$g^{ex} = \frac{a}{a_\infty} = \frac{h_\infty}{h} = \frac{1}{\tilde{h}}. \tag{103}$$

Substituting expression (103) into Eqn (99) with $\tilde{\Pi}'_1 = -\tilde{\alpha}'\theta^2$ gives the equation of state for a monolayer with van der Waals interactions

$$\tilde{\Pi}' = \int_0^\theta \frac{1 - \mathrm{d}\ln\tilde{h}/\mathrm{d}\ln\theta}{1 - \theta/\tilde{h}}\,\mathrm{d}\theta - \tilde{\alpha}'\theta^2. \tag{104}$$

The system of Eqns (102) and (104) completely describes the state of a non-ionised monolayer with variable orientation of particles. A general solution to this system of equations is problematic but analysis of these equations in the differential form [47, 51–53] revealed a trend for the kink points in the surface pressure isotherm. Namely, if the kink point corresponds to an orientation phase transition, the slope of the curve must be smaller in the region of greater θ values (see Fig. 4).

V. Conclusion

The proposed procedure for deriving the equation of state based on the exclusion factor exhibits high creativity. This approach allows not only new highly accurate equations to be derived but also permits a better understanding of the well-established equations of state (a remarkable example is provided by the van der Waals equation). As to the use of the fitting parameter in refining the equation for the whole density range, it is appropriate to make the following comments. First, many equations of state include unknown constants that are more precisely determined in experiments. This is common practice. Second, in order to pass a curve through ten points with high accuracy using only one fitting parameter, one must have a very good equation. Eventually, third, this is a specific trick due to the fact that the problem of dependence of the exclusion factor on the density of matter is still to be solved. To solve this problem, one must know how the degree of particle clustering depends on the particle concentration. At present, this problem has been intensively studied by the researchers working in the field of physical chemistry of solutions.

It should be emphasised that the theory considers the short-range forces related to the particle size but not the long-range forces (the corresponding part of the equation of state has its traditional form). Note that in experimental studies on the role of the attraction and repulsion constants researchers deal with their combination, so knowledge of one constant facilitates determination of the other. Thus, finding the repulsion constants is also of great importance for the attractive part of the equation of state. What kind of force is more important? It is known that at temperatures above the Boyle temperature the attractive forces are insignificant so the behaviour of the gas is governed by the repulsive forces. However, recently it was suggested that near the triple point the decisive role in molecular systems is played by the repulsive forces, the attractive forces serving to keep particles together.[79]

This review has been written with the financial support of the Programme 'Leading Scientific Schools' (Project No. 789.2003.3) and the Russian Foundation for Basic Research (Project No. 04-03-32134).

References

1. S M Walas *Phase Equilibria in Chemical Engineering* (Boston: Butterworth, 1985)
2. J V Sengers, R F Kayser, C J Peters, H J White Jr (Eds) *Equation of State for Fluids and Fluid Mixtures* Pts 1, 2 (Amsterdam: Elsevier, 2000)
3. M Planck *Sitz. Ber. Preuss. K. Akad. Wiss.* (32) 633 (1908)
4. H Reiss, H L Frisch, J L Lebowitz *J. Chem. Phys.* **31** 369 (1959)
5. H Reiss, in *Statistical Mechanics and Statistical Methods in Theory and Application* (Ed. U Landman) (New York: Plenum, 1977) p. 99
6. B J Alder, T E Wainwright *J. Chem. Phys.* **33** 1439 (1960)
7. R J Speedy, H Reiss *Mol. Phys.* **72** 999 (1991)
8. H Reiss *J. Phys. Chem.* **96** 4736 (1992)
9. D S Corti, H Reiss *Mol. Phys.* **95** 269 (1998)
10. S Sastry, T M Truskett, P G Debenedetti, S Torquato, F H Stillinger *Mol. Phys.* **95** 289 (1998)
11. H Reiss *J. Stat. Phys.* **100** 73 (2000)
12. D S Corti *J. Phys. Chem. B* **105** 11772 (2001)
13. D Henderson *Mol. Phys.* **87** 273 (1996)
14. M Barosova *Mol. Phys.* **87** 423 (1996)
15. E Enciso, N G Almarza, D S Calzas, M A Gonzalez *Mol. Phys.* **92** 173 (1997)
16. A Santos, S B Yuste, M Lupez De Haro *Mol. Phys.* **96** 1 (1999)
17. P Bartlett *Mol. Phys.* **97** 685 (1999)
18. J Largo, J R Solana *Mol. Phys.* **96** 1367 (1999)
19. D Cao, K-Y Chan, D Henderson, W Wang *Mol. Phys.* **98** 619 (2000)
20. E Santiso, E A Muller *Mol. Phys.* **100** 2461 (2002)
21. D Viduna, W R Smith *Mol. Phys.* **100** 2815 (2002)
22. D Viduna, W R Smith *Mol. Phys.* **100** 2903 (2002)
23. D Gazzillo, A Giacometti *Mol. Phys.* **100** 3307 (2002)
24. T Boublik *Mol. Phys.* **100** 3443 (2002)
25. P Kadlec, J Janecek, T Boublik *Mol. Phys.* **98** 473 (2000)
26. J H de Boer *The Dynamical Character of Adsorption* (Oxford: Clarendon Press, 1953)
27. V V Krotov *Kolloidn. Zh.* **47** 1075 (1985) [a]
28. V B Fainerman, E H Lucassen-Reynders, R Miller *Colloids Surf. A* **143** 141 (1998)
29. V B Fainerman, R Miller, E V Aksenenko *Adv. Colloid Interface Sci.* **96** 339 (2002)
30. J J Erpenbeck, M Luban *Phys. Rev. A* **32** 2920 (1985)
31. J J Weis *Mol. Phys.* **93** 361 (1998)
32. S Toxvaerd *Mol. Phys.* **95** 539 (1998)
33. C Barrio, J R Solana *Phys. Rev. E* **63** 011201 (2001)
34. H Schlacken, H-J Mogel, P Schiller *Mol. Phys.* **93** 777 (1998)
35. A Santos, M López De Haro, S Bravo Yuste *J. Chem. Phys.* **103** 4622 (1995)
36. M López De Haro, A Santos, S Bravo Yuste *Eur. J. Phys.* **19** 281 (1998)
37. A I Rusanov *Mendeleev Commun.* 11 (2003)
38. A I Rusanov *J. Chem. Phys.* **118** 10157 (2003)
39. A I Rusanov *Dokl. Akad. Nauk* **390** 62 (2003) [b]
40. A I Rusanov *Mendeleev Commun.* (5) 170 (2003)
41. A I Rusanov *Zh. Fiz. Khim.* **77** 1764 (2003) [c]
42. A I Rusanov *J. Chem. Phys.* **119** 10268 (2003)
43. A I Rusanov *Zh. Fiz. Khim.* **78** 234 (2004) [c]
44. A I Rusanov *Mendeleev Commun.* 107 (2004)
45. A I Rusanov *Dokl. Akad. Nauk* **396** 119 (2004) [b]
46. A I Rusanov *Mendeleev Commun.* 201 (2004)
47. A I Rusanov *Mendeleev Commun.* 218 (2002)
48. A I Rusanov *Mendeleev Commun.* 62 (2003)
49. A I Rusanov *Mendeleev Commun.* 241 (2003)
50. A I Rusanov *Mendeleev Commun.* 11 (2004)

51. A I Rusanov *Dokl. Akad. Nauk* **394** 347 (2004) [b]
52. A I Rusanov *Colloid. Surf.* **239** 105 (2004)
53. A I Rusanov *J. Chem. Phys.* **120** 10 736 (2004)
54. A I Rusanov *Zh. Fiz. Khim.* **78** 1351 (2004) [c]
55. J P M Trusler, in *Equation of State for Fluids and Fluid Mixtures* Pt. 1 (Eds J V Sengers, R F Kayser, C J Peters, H J White Jr) (Amsterdam: Elsevier, 2000) p. 35
56. H N V Temperley *Proc. Phys. Soc. A* **67** 233 (1954)
57. R Brout *Phase Transitions* (New York: Benjamin, 1965)
58. N A Smirnova, A I Viktorov, in *Equation of State for Fluids and Fluid Mixtures* Pt. 1 (Eds J V Sengers, R F Kayser, C J Peters, H J White Jr) (Amsterdam: Elsevier, 2000) p. 255
59. J J Erpenbeck, W W Wood *J. Stat. Phys.* **35** 321 (1984)
60. N F Carnahan, K E Starling *J. Chem. Phys.* **51** 635 (1969)
61. E Thiele *J. Chem. Phys.* **39** 474 (1963)
62. M S Wertheim *Phys. Rev. Lett.* **10** E501 (1963)
63. E A Guggenheim *Mol. Phys.* **9** 199 (1965)
64. F H Ree, W G Hoover *J. Chem. Phys.* **46** 4181 (1966)
65. E J Le Fevre *Nature, Phys. Sci.* **20** 235 (1972)
66. L V Woodcock *J. Chem. Soc., Faraday Trans. 2* **72** 731 (1976)
67. A I Rusanov *Zh. Fiz. Khim.* **79** (2) (2005) [c]
68. A I Rusanov *J. Chem. Phys.* **121** 1873 (2004)
69. C A Croxton *Liquid State Physics — A Statistical Mechanical Introduction* (Cambridge: Cambridge University Press, 1974)
70. E Helfand, H L Frish, J L Lebowitz *J. Chem. Phys.* **34** 1037 (1961)
71. H L Frish *Adv. Chem. Phys.* **6** 229 (1964)
72. D Henderson *Mol. Phys.* **30** 971 (1975)
73. F C Andrews *J. Chem. Phys.* **62** 272 (1975)
74. F C Andrews *J. Chem. Phys.* **64** 1941 (1976)
75. A Baram, M Luban *J. Phys. C* **12** L659 (1979)
76. J C Sanchez *J. Chem. Phys.* **101** 7003 (1994)
77. Y Hayami, A Uemura, N Ikeda, M Aratono, K Motomura *J. Colloid Interface Sci.* **172** 142 (1995)
78. S May, A Ben-Shaul *Biophys. J.* **76** 751 (1999)
79. H C Longuet-Higgins, B Widom *Mol. Phys.* **100** 23 (2002)

[a] — *Colloid J. (Engl. Transl.)*
[b] — *Dokl. Chem. (Engl. Transl.)*
[c] — *Russ. J. Phys. Chem. (Engl. Transl.)*