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Novel ideas on the equation of state

Anatoly I. Rusanov

Mendeleev Center, St. Petersburg State University, 199034 St. Petersburg, Russian Federation.
Fax: +7 812 428 6939; e-mail: rusanov@AR1047.spb.edu

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Up to the present time, the equation of state remains one of the central problems of science. A survey of recent work on a new thermodynamic approach to derive an equation of state for three- and two-dimensional systems of any nature is given; the best known equations of state acquire their location in the resultant hierarchy of approximations, and more precise equations of state are derived.

Every physicochemical state of matter is determined by the set of state parameters: temperature, pressure, density and composition. The significance of the equation of state originates from the fact that it relates the state parameters to each other. Finding the equation of state is one of central problems of the knowledge of nature and is under discussion in the literature since 1662 (the Boyle–Mariotte law). Nevetheless, interest in this problem only deepens, and it remains at the focus of modern science suggesting powerful computational methods.

Novel approaches were suggested to derive the main old-established and some new and more precise equations of state for bulk phases[1–6] and surface monolayers.[7–9] In both the cases, the general statistical-mechanical expression for the chemical potential of a particle (a molecule, an ion, or a colloidal nanoparticle) was used in the form

$$\mu_i = \mu_i^0 + k_B T \ln(c_i \Lambda_i^3), \tag{1}$$

where μ_i^0 is the chemical potential of a particle of sort i with resting centre of mass in a system under consideration, k_B is the Boltzmann constant, T is the temperature, c_i and Λ_i are the particle concentration and de Broglie wavelength (Λ_i is a function of temperature), respectively. The traditional term with an activity coefficient has been included in μ^0 whose only difference from μ is that μ^0 refers to a particle at rest. The use of equation (1) was different for the cases of a bulk phase and a monolayer. Therefore, both of the cases are separately considered below.

An equation of state for a bulk phase

Before we outline the theory, some new concepts and definitions should be considered. First of all, this is a new and rigorous thermodynamic definition of the excluded volume v_i^{ex} as the partial volume of a particle of sort i with resting centre of mass in the absence of all interactions except the short-range interaction related to the particle own volume:

$$v_i^{ex} \equiv v_i^0\Big|_{\text{No long-range forces}} \equiv \left(\frac{\partial V}{\partial N_i^0}\right)_{T,\,p,\,N_j,\,N^0_{j\neq i},\ \text{no long-range forces}}. \tag{2}$$

Here, v_i^0 is the partial volume of a resting particle of sort i defined as the derivative of the system volume V with respect to the number of resting particles N_i^0 in a system provided the system temperature T and pressure p, as well as the numbers of other particles N_j, $N^0_{j\neq i}$ are maintained constant. A similar definition for the partial particle volume v_i (related to ordinary, *i.e.*, moving particles) is well known in thermodynamics to obey the relationship

$$v_i = \left(\frac{\partial \mu_i}{\partial p}\right)_{T,\{x_i\}}, \tag{3}$$

where $\{x_i\}$ is the set of mole fractions symbolising the constancy of composition. The analogous equation for resting particles

$$v_i^0 = \left(\frac{\partial \mu_i^0}{\partial p}\right)_{T,\{x_i\}} \tag{4}$$

was deduced[2] as a new thermodynamic relationship.

For both resting and moving particles, the partial particle volume is different from the particle volume v_{i0}. In gases, for example, v_i is incomparably larger than v_{i0}. Moreover, the partial particle volume can be of any sign because of competition between repulsive and attractive forces. The latter belong to long-range forces whose absence makes the partial volume of a resting particle positive and equal to the excluded volume. Thus, the excluded volume is always positive and, in addition, comparable in dimensions with the particle volume. Indeed, the excluded volume is usually understood as a space inaccessible to the centres of mobile particles. Assuming particles to be spherical (for the reason of Brownian rotation or simply as a model) and the particle density to be small, the excluded volume can be estimated as described below. For moving particles of sort k with radius r_k, a single resting particle of sort i with radius r_i creates an excluded volume of v_{ik}^{ex} as a sphere of radius $r_i + r_k$ (Figure 1). This makes the relationship

$$v_{ik}^{ex} = (v_{i0}^{1/3} + v_{k0}^{1/3})^3, \tag{5}$$

where $v_{i0} = 4\pi r_i^3/3$ and $v_{k0} = 4\pi r_k^3/3$ are the corresponding

Dr. Rusanov is a professor of physical chemistry at the St. Petersburg State University, where he has been a Chemistry Faculty member since 1955 and head of the Department of Colloid Chemistry since 1987. Dr. Rusanov was elected to the Academy of Sciences of the USSR in 1990 and to the Russian Academy of Sciences (as a full member) in 1991.

His research interests are in colloid and interface science; the thermodynamics of solutions and interfaces; the physical chemistry of surfactants, micelles and vesicles, nucleation processes in phase transitions; surface separation science; mechanochemistry; and molecular dynamics. Rusanov has elaborated a thermodynamic and statistical theory of surface layers, formulated a number of general laws of surface phenomena: the generalised phase rule, the adsorption equation for solids and systems in an electric field, the Konovalov law analogues for interfaces, the generalised Gibbs–Curie principle, *etc*. He has proposed new methods for the investigation of interfaces such as the determination of surface layer thickness and the measurement of the surface density of matter. He has discovered and explained new phenomena: a dramatic increase in the surface layer thickness of a solution in contact with a gas when approaching the critical solution point, the anisotropy of wetting of deformed polymers, the effect of strain sign on the solubility of a solid, a higher temperature of maximum density of water at the surface, linear in charge effects in hydration and nucleation on charged centres, which initiates charge separation processes in the atmosphere.

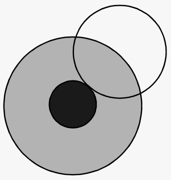

Figure 1 The excluded volume (shaded) created by a resting particle (black circle) with respect to a mobile particle (empty circle).

particle volumes. If all the particles are of the same volume, equation (5) shows the excluded volume to be eight times as large as the particle volume. This is the highest value for this ratio, which becomes smaller for mixtures. Averaging equation (5) yields the excluded volume for a gaseous mixture as

$$v^{\mathrm{ex}} = \sum_{i,k} x_i x_k (v_{i0}^{1/3} + v_{k0}^{1/3})^3. \tag{6}$$

Similarly, the average particle volume and the average partial particle volume in a mixture are

$$v_0 = \sum_i x_i v_{i0} \text{ and } v^0 = \sum_i x_i v_i^0, \tag{7}$$

respectively. The exclusion factor f, the most important parameter of the theory, is defined as the ratio between the average excluded volume and the average particle volume in a system

$$f \equiv v^{\mathrm{ex}}/v_0. \tag{8}$$

As it follows from (6) and (7), the exclusion factor f_0 for a rarified gaseous mixture can be easily calculated from the expression

$$f_0 = \frac{v^{\mathrm{ex}}}{v_0} = \frac{\sum_{i,k} x_i x_k (v_{i0}^{1/3} + v_{k0}^{1/3})^3}{\sum_i x_i v_{i0}}. \tag{9}$$

In particular, $f_0 = 8$ in the case of a one-component system. Passing from a rarified gas to denser states is accompanied by clustering, which leads to a decrease in the exclusion factor.[2,3] The lowest value is $f = 1$ for soft particles (capable of filling the space without cavities), and it is larger than unity for hard particles (depending on the type of packing). Generally,

$$f_0 \ge f \ge v_\infty/v_0, \tag{10}$$

where v_∞ is the limiting volume per particle in an infinitely large cluster. The equality of v_∞ and v_0 is possible only for soft particles. In other cases, v_∞ is typically larger than v_0. For hard spheres, for example, $v_\infty/v_0 = 6/\pi \approx 1.91$ at a cubic packing and $v_\infty/v_0 = 6/\pi\sqrt{2} \approx 1.35$ at a hexagonal packing. In any case, the exclusion factor is variable within a narrow range of $8 \ge f \ge 1$, whereas the pressure changes from zero to infinitely large values. This remarkable fact makes the exclusion factor a useful tool for constructing an equation of state.

The formulation of the theory begins with the derivation of a master equation, which is an exact and rigorous thermodynamic relationship to generate equations of state. We start with the Gibbs–Duhem equation

$$\mathrm{d}p = -s\,\mathrm{d}T + \sum_i c_i\,\mathrm{d}\mu_i, \tag{11}$$

where s is the entropy density and c_i is the concentration of particles of sort i. We shall integrate equation (11) at constant temperature and composition (this restriction will be cancelled after the integration). Then every concentration can be expressed through the total concentration $c = \sum_i c_i$ as $c_i = cx_i$ with constant x_i so that actually only c will be a variable of integration. Under this condition, putting (1) in (11) and accounting for (4), we obtain

$$\frac{\mathrm{d}p}{\mathrm{d}c} = \frac{k_\mathrm{B}T}{1 - cv^0}, \tag{12}$$

where v^0 is the average partial volume of a resting particle defined in equation (7). As was stated above, the behaviour of this quantity is too complicated to perform the integration of (12) in a general form. To overcome this difficulty, we integrate (12) in the absence of long-range forces [then v^0 is automatically replaced by v^{ex} according to definition (2)] but compensate this by adding a separate long-range term p_l to the final expression. This results in the master equation

$$p = k_\mathrm{B}T \int_0^c \frac{\mathrm{d}c}{1 - cv^{\mathrm{ex}}} + p_l\,. \tag{13}$$

The expressions for p_l can be found in the literature. For example,

$$p_l = -\sum_{i,k} \alpha_{ik} c_i c_k \tag{14}$$

for the case of van der Waals forces, when α_{ik} is the attraction constant for particles of sorts i and k.

For the sake of simplicity, master equation (13) is written in the dimensionless form

$$\tilde{p} = \int_0^\varphi \frac{\mathrm{d}\varphi}{1 - f\varphi} + \tilde{p}_l\,, \tag{15}$$

where $\tilde{p} \equiv pv_0/k_\mathrm{B}T$ and $\tilde{p}_l$ are the dimensionless pressure and its dimensionless long-range part, respectively, and $\varphi \equiv cv_0 = \sum_i c_i v_{i0} = \sum_i \varphi_i$ is the total packing fraction of all species as the sum of individual packing fractions φ_i. Correspondingly, equation (14) is transformed to

$$\tilde{p}_l = -\sum_{i,k} \tilde{\alpha}_{ik} \varphi_i \varphi_k \tag{16}$$

where $\tilde{\alpha}_{ik} \equiv \alpha_{ik} v_0/k_\mathrm{B}Tv_{i0}v_{k0}$ is the dimensionless form of the attraction constant α_{ik}. In the modern literature, the packing fraction φ is usually replaced by the reduced density $y \equiv \sigma^3/v = (6/\pi)\varphi$, where σ is the particle diameter. This corresponds to the cubic packing of hard spheres, which is not the densest packing. We define the reduced density more generally as $y \equiv v_\infty/v$ (where v_∞ may also belong to the hexagonal packing) to write a dimensionless form of the master equation as

$$\tilde{p}' = \int_0^y \frac{\mathrm{d}y}{1 - gy} + \tilde{p}_l', \tag{17}$$

where $\tilde{p}' \equiv pv_\infty/k_\mathrm{B}T$, and $g \equiv v^{\mathrm{ex}}/v_\infty$ is another exclusion factor. Correspondingly, the second dimensionless form for (14) is

$$\tilde{p}_l' = -\sum_{i,k} \tilde{\alpha}_{ik}' y_i y_k \tag{18}$$

with $\tilde{\alpha}_{ik}' \equiv \alpha_{ik} v_\infty/k_\mathrm{B}Tv_{i\infty}v_{k\infty}$ as a dimensionless attraction constant. The exclusion factor g becomes unity for the densest state, and, for this reason, equation (17) is more convenient for a condensed state of matter. However, as we started from a gaseous state, we shall deal mostly with equation (15).

The evaluation of the integral in (15) needs the knowledge of the $f(\varphi)$ function. Information on a one-component system can be obtained[1,2] from the first ten virial coefficients for a system of hard spheres tabulated in the literature[10] to imagine a descending concave curve for the plot $f(\varphi)$ (curve *4* in Figure 2). As for the general form of the $f(\varphi)$ function, it remains unknown up to the present. However, having in mind that the exclusion factor is capable of changing only within a very narrow range, we hope that some reasonable approximations for the $f(\varphi)$ function will result in sufficiently accurate equations of state.

The crudest zero approximation implies the exclusion factor f to be a constant. Master equation (15) then yields the equation of state

$$\tilde{p} = -\frac{\ln(1-f\varphi)}{f} + \tilde{p}_l\,. \tag{19}$$

Particular cases of this equation are well known. Applying equation (19) first to a nonionic monatomic gas with setting $f = 8$ and using (16), we arrive at the Planck equation of state[11] (written here in a dimensionless form)

$$\tilde{p} = -\frac{\ln(1-8\varphi)}{8} - \tilde{\alpha}\varphi^2. \tag{20}$$

The Planck equation correctly reproduces the first and second coefficients of the virial expansion for gases. Passing to a condensed state and taking the same approximation for equation (17) with $g = 1$ and using (18), we arrive at the equation of state

$$\tilde{p}' = -\ln(1-y) - \tilde{\alpha}'y^2. \tag{21}$$

An equation of this type was obtained[12,13] by applying the Ising model to the theory of condensation of a lattice gas. Later, equation (21) was often used in lattice models.[14]

The first approximation in equation (15) assumes a linear decrease of the exclusion factor

$$f = f_0 - k\varphi, \tag{22}$$

where f_0 is the exclusion factor for a rarified gas and k is a coefficient, which restricts the range of possible variations in φ. Putting (22) in (15) yields the equation of state in the first approximation

$$\tilde{p} = \int_0^{\varphi} \frac{\mathrm{d}\varphi}{1 - f_0\varphi + k\varphi^2} + \tilde{p}_l\,, \tag{23}$$

The result of integration in (23) not only numerically but also functionally depends on the k value chosen. At this stage, we also use the principle of maximum simplicity of a resultant equation of state, which leads to the unique value $k = (f_0/2)^2$ and to the equation of state

$$\tilde{p} = \frac{\varphi}{1-(f_0/2)\varphi} + \tilde{p}_l\,, \tag{24}$$

For a one-component system with $f_0 = 8$ and van der Waals forces [equation (16)], equation (24) takes the form

$$\tilde{p} = \frac{\varphi}{1-4\varphi} - \tilde{\alpha}\varphi^2,\;\; p = \frac{k_\mathrm{B}T}{v-4v_0} - \frac{\alpha}{v^2}\,, \tag{25}$$

which is the van der Waals equation of state (duplicated here in a traditional form). The result obtained is important for two reasons. First, it determines the place of the van der Waals equation in the hierarchy of approximations. Second, it explains misunderstanding $4v_0$ as a constant excluded volume, which was under discussion for many years. Indeed, 4 in (25) is necessary to produce a proper value for the second virial coefficient, whereas the excluded volume should be $8v_0$ for gases. Van der Waals himself erroneously explained this contradiction by the fact that two molecules participate in a collision and, therefore, 8 should be divided by two. We now see that, in reality, there is no constant value for the excluded volume in the van der Waals equation because the excluded volume is implied to be variable.

In the second approximation of the excluded volume theory,[1–6] the concavity of the $f(\varphi)$ curve is taken into account by introducing the linear-fractional function

$$f = \frac{f_0 - k_1\varphi}{1 + k_2\varphi}, \tag{26}$$

with two positive constants k_1 and k_2. One more positive constant K is introduced from the limiting slope for the $f(\varphi)$ function:

$$\left(\frac{\mathrm{d}f}{\mathrm{d}\varphi}\right)_{\varphi\to 0} = -K. \tag{27}$$

Using (26), we obtain the equation

$$k_1 + k_2 f_0 = K, \tag{28}$$

which relates coefficients k_1 and k_2 to each other, so that only one of them can be chosen independently.

After putting (26), equation (15) takes the form

$$\tilde{p} = \int_0^{\varphi} \frac{(1-k_2\varphi)\mathrm{d}\varphi}{1-(f_0-k_2)\varphi + k_1\varphi^2} + \tilde{p}_l\,. \tag{29}$$

The solution of (29) depends on the values chosen for coefficients k_1 and k_2. The simplest solution corresponds to the condition

$$k_1^{1/2} = \frac{f_0 - k_2}{2} \equiv \beta, \tag{30}$$

which, together with (28), uniquely determines coefficients k_1 and k_2:

$$k_1 = (f_0 - K^{1/2})^2,\;\; k_2 = 2K^{1/2} - f_0. \tag{31}$$

With these values of k_1 and k_2, (29) yields the equation of state

$$\tilde{p} = \frac{f_0-\beta}{\beta}\,\frac{\varphi}{1-\beta\varphi} + \frac{f_0-2\beta}{\beta^2}\ln(1-\beta\varphi) + \tilde{p}_l\,, \tag{32}$$

where $\beta = f_0 - K^{1/2}$. Equation (32) looks as a combination of the van der Waals and Planck equations. However, equation (32) is much more accurate than both the famous equations and exactly reproduces the first three virial coefficients.

For the case of a nonionic system with van der Waals forces, using (16), equation (32) can be written as

$$\tilde{p} = \frac{f_0-\beta}{\beta}\,\frac{\varphi}{1-\beta\varphi} + \frac{f_0-2\beta}{\beta^2}\ln(1-\beta\varphi) - \sum_{i,k}\tilde{\alpha}_{ik}\varphi_i\varphi_k\,. \tag{33}$$

For a one-component system, we have $f_0 = 8$, $K = 34$ and $\beta \approx 2.169$, and equation (33) takes the numerical form

$$\tilde{p} = \frac{2.688\varphi}{1-2.169\varphi} + 0.778\ln(1-2.169\varphi) - \tilde{\alpha}\varphi^2. \tag{34}$$

A comparison of the critical parameters of equation (34) and the Planck and van der Waals equations supplies a good illustration of ascending in the hierarchy of approximations.[1–6] As an example, Figure 2 shows how the range of applicability changes for the above three approximations. The outstanding parameter of equation (34) is the ratio between the Boyle temperature T_B and the critical temperature T_c: $T_\mathrm{B}/T_\mathrm{c} = 2.74$ against the experimental value 2.75.

An equation of state for a surface monolayer

A similar method was applied to the analysis of a surface monolayer (usually formed by adsorbed or spread matter) by replacing volume by area. It is misleading to think that passing

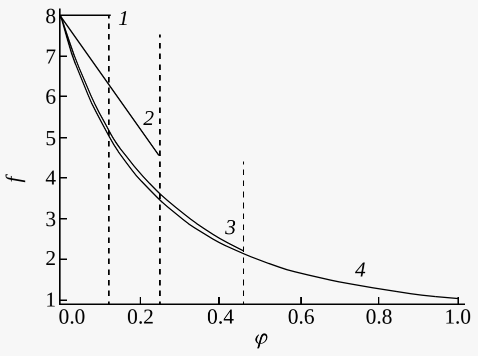

Figure 2 The dependence of the exclusion factor on the packing fraction (solid lines) and the limits of applicability for the corresponding state equations (dashed lines): *1* refers to the Plank equation, *2* refers to the van der Waals equation and *3* refers to equation (34); *4* is the line obtained from the virial expansion for hard spheres with known 10 coefficients.

from the equation of state for a bulk system to the equation of state for a monolayer is reduced to trivially lowering the dimensionality of a system. Considering non-spherical particles, the particle volume v_0 is independent of the particle orientation in space. By contrast, the particle parking area a_0 does depend on the particle orientation, and this is a source of complication. The orientation is often influenced by a substrate, which is beyond two-dimensional concepts. Generally, an adequate description of a monolayer requires a three-dimensional theory, and we shall use the same expression for the chemical potential as that for a three-dimensional system, equation (1).

We consider a multicomponent monolayer on a flat substrate that can be solid or liquid. Since we are interested in the interdependence of interfacial parameters only, the monolayer is assumed to be insoluble, which allows us to perform a rigorous analysis on the basis of equilibrium thermodynamics. The main thermodynamic relationship is the Gibbs adsorption equation

$$d\gamma = -\bar{s}dT - \sum_i \Gamma_i d\mu_i, \tag{35}$$

where γ is the surface tension, $\bar{s}$ is the excess entropy per unit area, Γ_i and μ_i are the adsorption (the excess amount per unit area) and chemical potential of particles of sort i present in the monolayer, respectively. The summation in (35) is carried out over all species of the monolayer, and it does not include the substrate. For insoluble monolayers, the adsorption Γ_i coincides with the real amount of a substance per unit monolayer area. In other words, Γ_i is the surface concentration of particles of sort i, which is related to the ordinary (three-dimensional) concentration as

$$c_i = \Gamma_i/h_i, \tag{36}$$

where h_i is the average dimension of particles of sort i in the direction normal to the monolayer plane. Obviously, h_i is sensitive to the particle orientation in the case of non-spherical particles.

According to the Gibbs adsorption equation, the presence of a monolayer on the substrate surface leads to a decrease of the surface tension. This decrease is designated as

$$\Pi \equiv \gamma_0 - \gamma, \tag{37}$$

where γ_0 is the surface tension of the pure substrate. Π is called surface pressure, which is the main characteristic of a monolayer. Putting (37) reduces (35) to the form resembling the Gibbs–Duhem equation (11):

$$d\Pi = \bar{s}dT + \sum_i \Gamma_i d\mu_i. \tag{38}$$

Equations (1), (36) and (38) make the base of the theory. In addition, we need some quantities and relationships of surface thermodynamics presented below.

The main surface characteristics of particles of sort i in a monolayer are the parking area a_{i0}, the minimum possible area per particle $a_{i\infty}$ (at $\Pi \to \infty$), the partial area a_i, the partial area of a particle at rest a_i^0, and the excluded area a_i^{ex} defined as the partial area of a particle at rest in the absence of long-range forces:[7–9]

$$a_i^{ex} \equiv a_i^0\Big|_{\text{No long-range forces}} \equiv \left(\frac{\partial A}{\partial N_i^0}\right)_{T,\,\Pi,\,N_j,\,N^0_{j\neq i},\,\text{no long-range forces}}, \tag{39}$$

where A is the monolayer area. The partial areas obey the relationships

$$a_i = \left(\frac{\partial \mu_i}{\partial \Pi}\right)_{T,\{x_i\}},\ \ a_i^0 = \left(\frac{\partial \mu_i^0}{\partial \Pi}\right)_{T,\{x_i\}}, \tag{40}$$

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

$$x_i = \Gamma_i/\Gamma,\ \ \Gamma = \sum_i \Gamma_i. \tag{41}$$

Of two equations (40), the latter was earlier unknown in surface thermodynamics.

Correspondingly to the above characteristics, average quantities for the whole multicomponent monolayer are introduced:

$$a_0 \equiv \sum_i x_i a_{i0}, \tag{42}$$

$$a_\infty \equiv \sum_i x_i a_{i\infty}, \tag{43}$$

$$a \equiv \sum_i x_i a_i, \tag{44}$$

$$a^0 \equiv \sum_i x_i a_i^0, \tag{45}$$

$$a^{ex} = \sum_i x_i a_i^{ex}. \tag{46}$$

In addition, averaging h_i leads to the quantity h

$$h \equiv \sum_i x_i h_i, \tag{47}$$

which can be interpreted as the average monolayer thickness.

Integrating equation (38) at constant temperature and composition with accounting for (1), (36) and (39)–(47), we come to the master equation

$$\Pi = k_B T \int_0^\Gamma \frac{1 - c\,dh/d\Gamma}{1 - \Gamma a^{ex}}\,d\Gamma + \Pi_l\,, \tag{48}$$

where Π_l is the long-range part of surface pressure. For example,

$$\Pi_l = -\sum_{i,k} \alpha_{ik}\Gamma_i\Gamma_k \tag{49}$$

for the case of van der Waals forces. Equation (48) is an analogue of master equation (13) for a bulk phase. However, equation (48) looks more complicated due to the orientation effect mirrored by the derivative $dh/d\Gamma$. If the particle orientation is fixed or if all particles are spherical, the derivative $dh/d\Gamma$ becomes zero, and master equation (48) acquires the two-dimensional form

$$\Pi = k_B T \int_0^\Gamma \frac{d\Gamma}{1 - \Gamma a^{ex}} + \Pi_l\,, \tag{50}$$

which is suitable for deriving two-dimensional equations of state.

Using a_0 or a_∞, equation (50) can be written in two alternative dimensionless forms. The first dimensionless form of the two-dimensional master equation is

$$\tilde{\Pi} = \int_0^\varphi \frac{d\varphi}{1 - f\varphi} + \tilde{\Pi}_l\,, \tag{51}$$

where $\tilde{\Pi} \equiv \Pi a_0/k_B T$ and $\tilde{\Pi}_l$ are the dimensionless surface pressure and its long-range part, respectively, $\varphi \equiv \Gamma a_0$ is the total surface packing fraction, and $f \equiv a^{ex}/a_0$ is an exclusion factor. The second dimensionless form of the two-dimensional master equation is

$$\tilde{\Pi}' = \int_0^\theta \frac{d\theta}{1 - g\theta} + \tilde{\Pi}'_l, \tag{52}$$

where the dimensionless surface pressure is expressed as $\tilde{\Pi}' \equiv \Pi a_\infty/k_B T$, $\theta \equiv \Gamma a_\infty$ is the surface coverage, and g is the second exclusion factor defined and related to f as

$$g \equiv a^{ex}/a_\infty = f a_0/a_\infty. \tag{53}$$

For van der Waals forces, the long-range terms in (51) and (52) are of the forms

$$\tilde{\Pi}_l = -\sum_{i,k} \tilde{\alpha}_{ik}\varphi_i\varphi_k, \tag{54}$$

$$\tilde{\Pi}'_l = -\sum_{i,k} \tilde{\alpha}'_{ik}\theta_i\theta_k, \tag{55}$$

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, equations (51) and (52) are equivalent and used for the reason of convenience. Equation (51) is more appropriate for gases, while equation (52) is more convenient for a condensed state. Since we start from gases, we shall use mostly equation (51).

The problem of finding the functions $f(\varphi)$ and $g(y)$ in (51) and (52) remains unsolved, but the limits of their variation have been established reliably.[8] In the gas limit, the average exclusion factor in a multicomponent monolayer is easily calculated as

$$f_0 = \frac{\sum\limits_{i,k} x_i x_k (a_{i0}^{1/2} + a_{k0}^{1/2})^2}{\sum\limits_i x_i a_{i0}}. \tag{56}$$

Equation (56) yields $f_0 = 4$ for a one-component monolayer and smaller values of f_0 for a mixed monolayer. These are the maximum possible values for the exclusion factor. The analysis of two-dimensional clustering[8] yields a minimum value of $f_\infty = a_\infty/a_0$ (depending numerically on the type of packing). Then, according to (53), a minimum value for g should be $g_\infty = 1$. In any case, the range of variation of the exclusion factor lies inside the range $4 > f$, $g > 1$, which is considerably narrower than that for three-dimensional systems. This promises a higher accuracy, as compared with three-dimensional systems, when representing the functions $f(\varphi)$ and $g(y)$ with approximations.

We now survey two-dimensional equations of state following from (51) and (52). The zero approximation implies a constant exclusion factor, which can be applied only to a small part of the state range, but both within gaseous and condensed state regions. Correspondingly, equations (51) and (52) yield

$$\tilde{\Pi} = -\frac{\ln(1 - f\varphi)}{f} + \tilde{\Pi}_l\,, \tag{57}$$

$$\tilde{\Pi}' = -\frac{\ln(1 - g\theta)}{g} + \tilde{\Pi}'_l. \tag{58}$$

For the case of a rarified pure non-ionised gas with $f = f_0 = 4$, with the use of (54), we can write equation (57) as

$$\tilde{\Pi} = -\frac{\ln(1 - 4\varphi)}{4} - \tilde{\alpha}\varphi^2. \tag{59}$$

This is a two-dimensional analogue of the Planck equation (20). Similarly to the Planck equation, equation (59) yields a proper value for the second virial coefficient of the two-dimensional virial expansion. Replacing 4 with f_0 given by (56), equation (59) acquires a generalised form for a gaseous mixture.

Equation (58) with $g = 1$ yields even two famous equations. Setting $\tilde{\Pi}'_l = 0$ leads to the van Laar equation of state for an ideal monolayer

$$\tilde{\Pi}' = -\ln(1 - \theta), \tag{60}$$

which is of the same form for one-component and mixed monolayers (the van Laar equation was first generalised by Krotov[15] for the multicomponent case). If we (again setting $g = 1$) represent $\tilde{\Pi}'_l$ according to (55), equation (58) yields

$$\tilde{\Pi}' = -\ln(1 - \theta) - \sum_{i,k} \tilde{\alpha}'_{ik}\theta_i\theta_k. \tag{61}$$

Equation (61) is a dimensionless form of the generalised Frumkin equation derived recently by Fainerman *et al.*:[16]

$$\Pi = -\frac{kT}{a_\infty}\ln\Big(1 - \sum_i \theta_i\Big) - \sum_{i,k} \alpha'_{ik}\theta_i\theta_k, \tag{62}$$

where $\alpha'_{ik} \equiv \alpha_{ik}/a_{i\infty}a_{k\infty}$. Proceeding to the case of a single species, equation (61) changes to the classical Frumkin equation (in a dimensionless form)

$$\tilde{\Pi}' = -\ln(1 - \theta) - \tilde{\alpha}'\theta^2. \tag{63}$$

In turn, the Frumkin equation changes to the van Laar equation at $\tilde{\alpha}' = 0$.

Starting from a gaseous state, we can set that, in the first approximation, the exclusion factor f is a linearly decreasing function of φ:

$$f = f_0 - k_1\varphi, \tag{64}$$

where k_1 is a positive constant. After putting (64) in (51), the simplest result follows with $k_1 = f_0^2/4$:

$$\tilde{\Pi} = \frac{\varphi}{1 - (f_0/2)\varphi} + \tilde{\Pi}_l. \tag{65}$$

Putting (54) converts (65) to the dimensionless generalised two-dimensional van der Waals equation

$$\tilde{\Pi} = \frac{\varphi}{1 - (f_0/2)\varphi} - \sum_{i,k} \tilde{\alpha}_{ik}\varphi_i\varphi_k. \tag{66}$$

With $f_0 = 4$ for a one-component monolayer, equation (66) acquires its classical form

$$\tilde{\Pi} = \frac{\varphi}{1 - 2\varphi} - \tilde{\alpha}\varphi^2. \tag{67}$$

Proceeding to the second approximation allows us to derivate a new two-dimensional equation of state.[7,8] The derivation is the same as given above for the three-dimensional case [equations (27)–(32)]. Starting with the condition expressed in (27), it results in the two-dimensional equation of state

$$\tilde{\Pi} = \frac{f_0 - \beta}{\beta}\,\frac{\varphi}{1 - \beta\varphi} + \frac{f_0 - 2\beta}{\beta^2}\ln(1 - \beta\varphi) + \tilde{\Pi}_l\,, \tag{68}$$

where $\beta = f_0 - K^{1/2}$. Equations (32) and (68) look similarly but differ in numerical coefficients. For the case of a nonionic monolayer with van der Waals forces, putting (54) gives a more detailed form of the equation of state as

$$\tilde{\Pi} = \frac{f_0 - \beta}{\beta}\,\frac{\varphi}{1 - \beta\varphi} + \frac{f_0 - 2\beta}{\beta^2}\ln(1 - \beta\varphi) - \sum_{i,k} \tilde{\alpha}_{ik}\varphi_i\varphi_k. \tag{69}$$

For a one-component monolayer, we have[8] $f_0 = 4$, $K = 6.616$ and $b = 1.428$. With these values, equation (69) acquires the numerical form

$$\tilde{\Pi} = \frac{1.801\varphi}{1 - 1.428\varphi} + 0.561\ln(1 - 1.428\varphi) - \tilde{\alpha}\varphi^2. \tag{70}$$

Equation (70) is a two-dimensional state equation in the second approximation. Unfortunately, a two-dimensional gaseous state has been studied not so thoroughly as a three-dimensional state. However, we can compare equation (70), to estimate its significance, with two-dimensional van der Waals equation (67), on one hand, and, on the other hand, with the hard discs model, for which there are exact parametric values in the literature.[17] The applicability range is wider for equation (70) ($0 < \theta < 0.7$) than that for the van der Waals equation ($0 < \theta < 0.5$), and equation (70) is considerably more exact. In contrast with the van der Waals equation giving correctly only the first and the second virial coefficients, equation (70) yields exact values for the first, second and third virial coefficients, an almost exact (only 9% higher) value for the fourth virial coefficient, and a value 28% higher for the fifth one.

It is also interesting to compare equations (34) and (70). Equation (70) is indeed more accurate than equation (34). Up to a recent time, only the van der Waals equation was equally known for three- and two-dimensional systems, and it was used to relate the properties of a substance in three- and two-dimensional states to each other. In particular, as de Boer[18] showed, the two-dimensional critical temperatures $T_c^{(2)}$ should be half as much as the three-dimensional critical temperature $T_c^{(3)}$ for the same substance. We now have a pair of much more accurate two-dimensional and three-dimensional equations of the same type, (34) and (70), to verify this rule. The corresponding computation[9] leads to the result

$$T_c^{(2)}/T_c^{(3)} \approx 0.455. \tag{71}$$

Equation (71) shows that de Boer's estimation $T_c^{(2)}/T_c^{(3)} \approx 0.5$ is almost correct but crude.

We return to equation (48) to discuss the role of orientation in the equation of state. Reasonably, if the particle orientation occurs, the main tendency is that the average monolayer thickness h increases with the surface concentration Γ as it simply follows from the balance of mass. If, however, $dh/d\Gamma > 0$, and the absolute value of the derivative is large enough, the instability condition $d\Pi/d\Gamma < 0$ can occur. As a result, a van der Waals loop can appear in the Π–Γ isotherm, which causes a first-order phase transition. Thus, the first and very fundamental conclusion that follows from equation (48) predicts the possibility of a two-dimensional first-order phase transition as a consequence of surface orientation. Remarkably, this prediction is valid even in the absence of attraction between anisometric particles (say, in a system of hard rods). The influence of orientation on the two-dimensional condensation was found in experiments with surfactant monolayers.[19]

To make equation (48) complete, we have to determine the dependence of the monolayer thickness on the surface concentration, which can be termed as an orientation equation of state. The problem of an orientation equation was unexplored, and only first steps were made recently.[7] The role of orientation in phase transitions (including second-order phase transitions) is especially important for a condensed state, where the methods of the theory of elasticity can be used. An approach of this type was applied, for example, to the theory of membranes by introducing a 'tilt modulus'.[20] Let us assume that a monolayer acquires elastic properties after exceeding a threshold surface concentration Γ_t. Within the frames of the theory of elasticity, the transversal elasticity modulus λ can be defined for a monolayer as

$$\lambda = \mathrm{d}(\Pi/h)/\mathrm{d}\ln h, \tag{72}$$

where Π/h is the tangential stress in the monolayer. Integrating (72) yields the orientation equation of state

$$\Pi = \Pi_t h/h_t + \lambda h \ln(h/h_t), \tag{73}$$

where the particular values Π_t and h_t correspond to Γ_t and to the transition to an elastic orientation, respectively. Such transition is usually seen as a kink point in the Π–Γ isotherm (Figure 3).

A general solution to the set of equations (48) and (73) is problematic. Some results were obtained from the analysis of these equations in the differential form.[7] In particular, equations (48) and (73) predict the shape of the Π–Γ isotherm in the case of a second-order phase transition caused by orientation (Figure 3): the isotherm slope should be smaller on the side of larger values of the surface concentration.

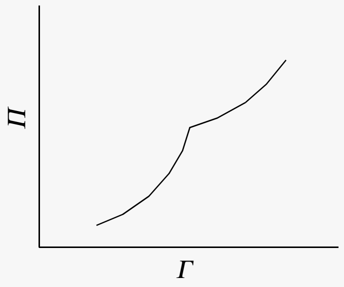

Figure 3 The Π–Γ isotherm at the point of an orientation two-dimensional second-order phase transition.

Conclusion

Note that the novel approach to an equation of state described above exhibits its high creativity. On one hand, this approach yields a better understanding of the most famous old-established equations of state as belonging to the bottom of the approximation hierarchy. On the other hand, new and more accurate equations of state have been derived. We stopped at the second approximation, but ascending the approximation hierarchy can be continued to obtain a universal equation of state for the whole density range in the future. Second, the approach based on the excluded volume and area improves only the repulsive part of an equation of state. However, this is important for both parts of the equation since an exact knowledge of the repulsive part will enhance better estimating the attractive part from experimental data.

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