Mendeleev Commun., 2003, 13(2), 62–63

Influence of clustering on a two-dimensional state equation

Anatoly I. Rusanov

Mendeleev Center, St. Petersburg State University, 199034 St. Petersburg, Russian Federation.
Fax: +7 812 428 6939; e-mail: rusanov@rus.usr.pu.ru

10.1070/MC2003v013n02ABEH001711

A general master equation accounting for the concentration dependence of the excluded area is presented, whose particular results are the two-dimensional van der Waals equation of state as the first approximation and a new much more precise state equation as the second approximation.

Recently,[1] we formulated the method of deriving a two-dimensional state equation on the basis of the excluded area. The master equation can be written in the form

$$(1-\sum_i \Gamma_i a_i)\mathrm{d}\Pi = kT\sum_i \Gamma_i \mathrm{d}\ln(\Gamma_i/h), \tag{1}$$

where Γ_i is the number of molecules of the ith component per unit area (for an insoluble monolayer, Γ_i coincides with the excess adsorption irrespective of the dividing surface location), a_i is the partial area of a resting molecule of the ith component (this quantity was also designated as an excluded area,[1] but we now distinguish a partial molecular area from an excluded area unless avoiding attractive forces in the system), kT is of the ordinary meaning, and h is the thickness of a monolayer under consideration. We introduce the total number of molecules of all species per unit area Γ and the average partial molecular area a

$$\Gamma \equiv \sum_i \Gamma_i,\ a \equiv \sum_i \Gamma_i a_i/\Gamma \tag{2}$$

to rewrite (1) as

$$(1-\Gamma a)\mathrm{d}\Pi = kT\mathrm{d}\Gamma - kT\Gamma\mathrm{d}\ln h. \tag{3}$$

They usually also introduce the parking areas a_{i0} of molecules and the parking area fractions $\theta_i \equiv \Gamma_i a_{i0}$. Operating with the average parking area a_0 in a multicomponent system, the degree of surface coverage θ, and the dimensionless image $\tilde{\Pi}$ of two-dimensional pressure

$$a_0 \equiv \sum_i \Gamma_i a_{i0}/\Gamma = \theta/\Gamma,\ \theta \equiv \sum_i \theta_i,\ \tilde{\Pi} \equiv \Pi a_0/kT, \tag{4}$$

we can represent equation (3) in the form

$$(1-\theta a/a_0)\mathrm{d}\tilde{\Pi} = \mathrm{d}\theta - \theta\mathrm{d}\ln h. \tag{5}$$

The procedure of deriving a state equation implies that equation (5) is integrated under the condition as if there were no attractive forces whose contribution (well known for molecular forces) will be then added explicitly to the final expression for two-dimensional pressure. Defining excluded area a^{ex} as the partial area of a resting molecule in the absence of attractive forces, the quantity a in equation (5) is replaced by a^{ex} in the course of integration. As a result, the procedure yields the final master equation

$$\tilde{\Pi} = \int_0^\theta \left(1-\frac{\mathrm{d}\ln h}{\mathrm{d}\ln\theta}\right)\frac{\mathrm{d}\theta}{1-\theta f^{\mathrm{ex}}} - \sum_{i,k}\alpha_{ik}\theta_i\theta_k, \tag{6}$$

where $f^{\mathrm{ex}} = a^{\mathrm{ex}}/a_0$ is the ratio of the excluded area to the parking area a_0 of a molecule, and α_{ik} is the constant of molecular attraction between the ith and kth species, the integration being carried out neglecting attractive forces but accounting for the real molecular structure of the system. We term f^{ex} the (area) exclusion factor. This dimensionless quantity will play a central role in the subsequent consideration.

The variety of areas introduced possibly needs some explanation. A parking area is known to be the smallest area needed to place a molecule on the surface. It simply coincides with a molecular dimension in the case of non-localised adsorption. An excluded area is the area inaccessible for the centers of moving molecules when a single molecule is at rest and does not attract other molecules. In other words, the excluded area results from molecular dimensions only. As for a partial molecular area strictly defined in thermodynamics, it is a more complex quantity depending on all kinds of molecular interaction. We have excluded this quantity from further consideration and will deal with only the ratio of the two simplest excluded and parking areas, denoted as the exclusion factor in equation (6).

Master equation (6) is to be used for deriving a state equation with accounting for both the excluded area and the monolayer thickness. The latter can be influenced by molecular orientation if it occurs as surface concentration changes. The effect of molecular orientation on two-dimensional pressure was analysed earlier.[1] To make clear other effects, we set the monolayer thickness to be constant. Omitting the term $d\ln h/d\ln\theta$ in (6), we write the master equation for the subsequent analysis in the form

$$\tilde{\Pi} = \int_0^\theta \frac{\mathrm{d}\theta}{1-\theta f^{\mathrm{ex}}} - \sum_{i,k}\alpha_{ik}\theta_i\theta_k. \tag{7}$$

Earlier, we neglected surface clustering (molecular aggregation) and considered the exclusion factor as a constant. Generally, this is not the case, especially for non-localised adsorption. We now show that clustering leads to the dependence of the exclusion factor on the degree of surface coverage.

A single molecule with a resting centre of mass is capable to rotation; therefore, it may be considered as having a round shape with radius r to be determined from the parking area as $a_0 = \pi r^2$. Insertion of such a molecule in a system creates the excluded area (inaccessible for the centres of mass of other molecules) $\pi(r+r)^2 = 4a_0$, so that $f^{\mathrm{ex}} = 4$.[1] This situation is typical of a rarefied two-dimensional gas consisting of insulate molecules. However, the situation changes when clustering occurs. The parking area of a cluster of radius R containing n molecules is $na_0 = n\pi r^2 = \pi R^2$, so that $R = rn^{1/2}$. The insertion of the cluster in the system creates the excluded area

$$na^{\mathrm{ex}} = \pi(R+r)^2 = \pi r^2(\sqrt{n}+1)^2 = a_0(\sqrt{n}+1)^2. \tag{8}$$

Thus, we have

$$f^{\mathrm{ex}} = \frac{(\sqrt{n}+1)^2}{n} = 1 + 2n^{-1/2} + n^{-1}. \tag{9}$$

Equation (9) shows the exclusion factor to decrease smoothly from a value of 4 at $n = 1$ to unity at $n = \infty$.

This conclusion can be verified using the virial expansion of the two-dimensional pressure of hard discs[2]

$$\Pi = kT(\Gamma + B_2\Gamma^2 + B_3\Gamma^3 + \ldots) \tag{10}$$

or

$$\tilde{\Pi} = \theta + \frac{B_2}{a_0}\theta^2 + \frac{B_3}{a_0^2}\theta^3 + \ldots = \theta + b_2\theta^2 + b_3\theta^3 + \ldots, \tag{11}$$

where B_i and b_i are virial coefficients for Π and $\tilde{\Pi}$, respectively. The known values of the second and third virial coefficients are $B_2 = 2a_0$ and $B_3 = 0.78200B_2^2$ (as computed by Tonks[2,3]). Correspondingly, we have $b_2 = 2$ and $b_3 = 0.782\times4 = 3.128$. As applied to the system of hard discs, master equation (7) yields

$$f^{\mathrm{ex}} = \left(\frac{\mathrm{d}\tilde{\Pi}}{\mathrm{d}\theta} - 1\right)\Big/\theta\frac{\mathrm{d}\tilde{\Pi}}{\mathrm{d}\theta} = \frac{2b_2 + 3b_3\theta + \ldots}{1 + 2b_2\theta + \ldots}, \qquad (12)$$

and we obtain the values $f^{\mathrm{ex}} = 4$ at $\theta = 0$ and $f^{\mathrm{ex}} = 1$ at $\theta = 1$ (the latter result is not influenced by the fact that the virial expansion diverges as $\theta \to 1$). Using the above values for b_2 and b_3, we found from (12) that

$$\left.\frac{\mathrm{d}f^{\mathrm{ex}}}{\mathrm{d}\theta}\right|_{\theta\to 0} = 3b_3 - 4b_2^2 = -6.616. \qquad (13)$$

Now, we proceed to estimating the integral in master equation (7). The case of the constancy of f^{ex} was considered earlier[1] and may be qualified as the zero approximation. Passing to the first (still sufficiently rough) approximation, we postulate $f^{\mathrm{ex}}(\theta)$ as the linearly decreasing function

$$f^{\mathrm{ex}} = 4 - k\theta, \qquad (14)$$

where k is a positive constant. Putting (14) in (7) makes the integrand $(1 - 4\theta + k\theta^2)^{-1}$. The form of a function resultant from integration depends on the k value. It may be chosen, for example, as satisfying equation (13). In this case, however, the state equation is practical in the narrow range of small θ and, in addition, looks rather awkward mathematically. The simplest result corresponds to $k = 4$, when the above trinomial changes to the square of a sum. In this case, we arrive at the state equation

$$\tilde{\Pi} = \frac{\theta}{1 - 2\theta} - \sum_{i,k}\alpha_{ik}\theta_i\theta_k, \qquad (15)$$

which is nothing else as the two-dimensional van der Waals equation in a generalised form (for a multicomponent system).

In the second approximation, we try to approach the real behaviour of the $f^{\mathrm{ex}}(\theta)$ function by accounting for its graphic concavity. We represent it as the linear-fractional function

$$f^{\mathrm{ex}} = \frac{4 - k_1\theta}{1 + k_2\theta} \qquad (16)$$

with two positive constants k_1 and k_2. To satisfy the requirement expressed in (13), the relationship holds $k_1 = 6.616 - 4k_2$ so that (16) can be written as

$$f^{\mathrm{ex}} = \frac{4 - (6.616 - 4k)\theta}{1 + k\theta}, \qquad (17)$$

where $k \equiv k_2$. Putting (17) in (7) changes the master equation to the form

$$\tilde{\Pi} = \int_0^\theta \frac{(1 + k\theta)\mathrm{d}\theta}{1 + (k - 4)\theta + (6.616 - 4k)\theta^2} - \sum_{i,k}\alpha_{ik}\theta_i\theta_k. \qquad (18)$$

Not only the numerical result of integration but also the resultant function depend on the k value chosen. The simplest form corresponds to the value $k = k_0$ satisfying the condition $(k_0 - 4)^2 = 4(6.616 - 4k_0)$, which yields $k_0 = -4 + 4(1.654)^{1/2} \approx \approx 1.144$. With $k = k_0$ equation (18) takes the form

$$\tilde{\Pi} = \frac{2\beta + 4}{\beta^2}\ln(1 + \beta\theta) - \frac{\beta + 4}{\beta}\,\frac{\theta}{1 + \beta\theta} - \sum_{i,k}\alpha_{ik}\theta_i\theta_k, \qquad (19)$$

where $\beta \equiv k_0/2 - 2 \approx -1.428$. With this approximate value of β, equation (19) numerically looks as

$$\tilde{\Pi} = 0.561\ln(1 - 1.428\theta) + 1.801\theta/(1 - 1.428\theta) - \sum_{i,k}\alpha_{ik}\theta_i\theta_k. \qquad (20)$$

Equation (19) is the two-dimensional state equation in the second approximation. Unfortunately, the two-dimensional gaseous state has been studied not so thoroughly as the three-dimensional one. However, we can compare equation (19), to estimate its significance, with van der Waals equation (15), on the one hand, and, on the other hand, with the hard discs model for which exact parametric values were published.[2] The applicability range is wider for equation (19) ($0 < \theta < 0.7$) than for the van der Waals equation ($0 < \theta < 0.5$), and equation (19) is considerably more exact. In contrast with the van der Waals equation, giving correctly only the first and the second virial coefficients, equation (19) yields exact values for the first, second and third virial coefficients, almost exact (only by 9% higher) value for the fourth virial coefficient, and a value by 28% higher for the fifth one. These outstanding characteristics of equation (19) can be complemented by the fact that equation (19) is a direct analogue of a recently derived three-dimensional state equation,[4] which was qualified as a precise state equation for a fluid.

This work was supported by the Russian Foundation for Basic Research (grant no. 01-03-32334).

References

1 A. I. Rusanov, *Mendeleev Commun.*, 2002, 218.
2 C. A. Croxton, *Liquid State Physics – A Statistical Mechanical Introduction*, Cambridge University Press, Cambridge, 1974.
3 L. Tonks, *Phys. Rev.*, 1936, **50**, 955.
4 A. I. Rusanov, *Mendeleev Commun.*, 2003, 11.

Received: 13th January 2003; Com. 03/2037