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Two-dimensional fluid equation of state for the entire range of surface densities

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A precise equation of state of a monolayer for the entire range of surface densities is derived as the third approximation of the theory of excluded area using a database for the model of hard disks.

Recently,[1,2] we formulated a method for deriving a two-dimensional equation of state on the basis of the exclusion factor $f \equiv a^{\text{ex}}/a_0$ (a^{ex} is the excluded area and a_0 is the parking area of particles forming a surface monolayer). For a one-component monolayer in the absence of orientation effects, the dimensionless master equation generating equations of state was obtained in the form

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

where $\varphi \equiv \Gamma a_0$ is the surface packing fraction (designated earlier as θ; Γ is the number of particles per unit monolayer area), $\tilde{\Pi} \equiv \Pi a_0/k_{\text{B}}T$ is the dimensionless two-dimensional pressure (Π is the surface pressure, k_{B} is the Boltzmann constant, and T is the temperature), and $\tilde{\Pi}_l$ is the long-range part of the two-dimensional pressure, including all forces except for those related to particle dimensions. In a particular case of molecular (van der Waals) forces, $\tilde{\Pi}_l$ is

$$\tilde{\Pi}_l = -\tilde{\alpha}\varphi^2, \tag{2}$$

where $\tilde{\alpha}$ is a dimensionless attraction constant.

The $f(\varphi)$ function is known[2] to represent a concavely decreasing dependence within the narrow interval $4 \geq f > 1$. This makes possible evaluating the integral in equation (1) in a more or less accurate way by approximating $f(\varphi)$ with simple algebraic functions. We analysed the case of constancy of f as the zero approximation, a linear decrease of f as the first approximation and the linear-fractional function

$$f = \frac{4 - k_1\varphi}{1 + k_2\varphi} \tag{3}$$

as the second approximation. Correspondingly, the equation of state in the second approximation as a simplest solution of master equation (1) was

$$\tilde{\Pi} = \frac{4 - 2\beta}{\beta^2}\ln(1 - \beta\varphi) + \frac{4 - \beta}{\beta}\,\frac{\varphi}{1 - \beta\varphi} + \tilde{\Pi}_l\,. \tag{4}$$

The coefficients in equations (3) and (4) were chosen to reproduce exactly the first, second and third virial coefficients, which finally resulted in the value $\beta \approx 1.428$. Thus, one can say that equation (4) is a gaseous equation by its origin.

To derive an equation of state for the entire range of surface densities, one has to deal with the set of data for the whole range rather than with the virial expansion. For the model of hard disks, such a set of data was obtained by Erpenbeck and Luban,[3] who computed 10 points of the equation of state using Monte Carlo and molecular dynamics simulations. Table 1 shows these data recalculated to our dimensionless variables. This database can be efficiently used for improving the procedure of deriving an equation of state within the theory of excluded area.

Let us begin with equation (4). One can see that equation (4) reproduces an exact value for the second virial coefficient (which secures its applicability to the gaseous state) irrespective of the value of β. Thus, we can try to improve equation (4) by converting β into a variable parameter to adjust equation (4) with $\tilde{\Pi}_l = 0$ to the above database. The best fit corresponds to $\beta \approx 1.2258$ (with the coefficient of determination 0.998154), so that equation (4) changes to the numerical form

$$\tilde{\Pi} = 1.0305\ln(1 - 1.2258\varphi) + \frac{2.263175\varphi}{1 - 1.2258\varphi} + \tilde{\Pi}_l\,. \tag{5}$$

Setting $\tilde{\Pi}_l = 0$, the corresponding $\tilde{\Pi}$ values from equation (5) and their deviations (%) from the database are displayed in Table 1. The maximal deviation is about 5.3%.

To derive a more precise equation of state, we consider the third approximation of the theory of excluded area. However, we shall not adjust the constants to virial coefficients. Passing from the second approximation to the third one, equation (3) changes to

$$f^{\text{ex}} = \frac{4 - k_1\varphi + k_3\varphi^2}{1 + k_2\varphi}, \tag{6}$$

where k_3 is a (still unknown) constant. Putting (6) in equation (1), we obtain

$$\tilde{\Pi} = \int_0^{\varphi} \frac{(1 + k_2\varphi)\mathrm{d}\varphi}{1 - (4 - k_2)\varphi + k_1\varphi^2 - k_3\varphi^3} + \tilde{\Pi}_l\,. \tag{7}$$

Following again the principle of maximal simplicity, we set $k_1 = 3k^2$, $k_2 = 4 - 3k$, and $k_3 = k^3$ to convert the denominator in (7) to $(1 - k\varphi)^3$, where k is a new constant. Putting all the values in equation (7) and performing integration lead to the equation of state in the third approximation

$$\tilde{\Pi} = \frac{\varphi - 2(k - 1)\varphi^2}{(1 - k\varphi)^2} + \tilde{\Pi}_l\,. \tag{8}$$

Remarkably, equation (8) is even simpler in form than the equation of state in the second approximation, equation (4), and, similarly to it, produces an exact value for the second virial coefficient (2 for the model of hard disks) irrespective of the value of constant k. This secures the applicability of equation (8) to a gaseous state at any value of k and permits the improvement of equation (8) by choosing a value of k to fit the database. The corresponding procedure yields the value $k \approx 1.0145$. With this value of k and $\Delta\tilde{\Pi} = 0$, equation (8) covers all the ten points of Erpenbeck and Luban with a high precision (the coefficient of determination is 0.999908). Numerically, equation (8) acquires the form

$$\tilde{\Pi} = \frac{\varphi - 0.029\varphi^2}{(1 - 1.0145\varphi)^2} + \tilde{\Pi}_l\,. \tag{9}$$

The $\tilde{\Pi}$ values produced by equation (9) at $\tilde{\Pi}_l = 0$ are shown in Table 1. The maximal deviation (Table 1) is about 1%. Thus, equation (9) is a precise equation of state.

Since the k value found is very close to unity, there is only a little loss of accuracy if setting $k = 1$. Equation (8) then becomes

$$\tilde{\Pi} = \frac{\varphi}{(1 - \varphi)^2} + \tilde{\Pi}_l \tag{10}$$

and exhibits an impressive combination of simplicity and accuracy. We do not represent a graphical comparison of equations (5), (9), (10), and the database since their plots would be very close to each other and scarcely distinguishable. However, Table 1 shows that equation (10) with $\tilde{\Pi}_l = 0$ remains more precise (with deviations from the database not exceeding 3.2%) as compared with equation (5) and, together with equation (9), is also to be referred to as the third approximation of the theory of excluded area.

Table 1 The values of dimensionless surface pressure from equations (5), (9) and (10) with $\tilde{\Pi}_l = 0$ as compared with a database for hard disks.[3]

φ	$\tilde{\Pi}$ (ref. 3)	$\tilde{\Pi}$ [equation (4)]	Deviation (%)	$\tilde{\Pi}$ [equation (9)]	Deviation (%)	$\tilde{\Pi}$ [equation (10)]	Deviation (%)
0.030230	0.032146	0.032137	0.027	0.032145	0.002	0.032144	0.005
0.045345	0.049763	0.049731	0.065	0.049758	0.010	0.049755	0.016
0.090690	0.109797	0.109477	0.29	0.109711	0.078	0.109682	0.10
0.181380	0.271764	0.268727	1.1	0.270976	0.29	0.270661	0.41
0.302301	0.627915	0.609889	2.9	0.623379	0.72	0.621015	1.1
0.453451	1.552766	1.474193	5.1	1.534743	1.16	1.518000	2.2
0.503834	2.101765	1.991259	5.3	2.077429	1.16	2.046606	2.6
0.566814	3.115412	2.980157	4.3	3.086957	0.91	3.020583	3.0
0.604601	3.994878	3.892926	2.6	3.973663	0.53	3.867215	3.2
0.647787	5.380584	5.490402	2.0	5.408334	0.51	5.221815	2.9

For the case of molecular forces, putting (2) in (10) results in the equation of state

$$\tilde{\Pi} = \frac{\varphi}{(1-\varphi)^2} - \tilde{\alpha}\varphi^2, \qquad (11)$$

which looks attractively because of its simplicity. Similarly to equation (9), equation (11) describes the state of a monolayer in the entire range of surface densities. It can also be applied to a critical state. By equating the first and second derivatives of $\tilde{\Pi}$ to zero, we obtain the critical values $\varphi_c \approx 0.215$, $\tilde{\alpha}_c \approx 5.841$, $\tilde{\Pi}_c \approx 0.0789$ and $\tilde{\Pi}_c/\varphi_c = 0.366$ (compressibility factor). The critical parameters of equation (11) seem no better than those of gaseous equations of state [for example, of equation (4)], but equation (11) has an advantage to be valid throughout the whole surface density range.

Note that the above consideration did not include the effect of molecular orientation, which is especially important for surfactant monolayers and is responsible for a number of additional phase transitions. Changing orientation results in a jump of the molecular area, so that equation (11) is capable of mirroring such phase transitions as breakpoints in the surface pressure isotherm. However, such characteristics are not complete because there should be an additional orientation term in the equation of state as it was discussed earlier.[1]

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