Comments on the Thermodynamic Justification of an Equation of State for Monolayers

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It is trivial to say that the excluded volume is of fundamental importance for the formulation of an equation of state, and the same can be said about the excluded area in the two-dimensional case. However, it was attempted[1] to derive an equation of state for a monolayer purely thermodynamically, with no use of the above important concept. The starting relationships were the Gibbs adsorption equation

$$d\gamma = -\sum_i \Gamma_i d\mu_i \tag{1}$$

and the known expression for the chemical potential in the surface layer

$$d\mu_i = RT \, d \ln(f_i^s x_i^s) - \omega_i \, d\gamma \tag{2}$$

where γ is surface tension, $\Gamma_i, \mu_i, f_i^s, x_i^s$ and ω_i are the adsorption (really, the number of molecules per unit area in an insoluble monolayer), chemical potential, surface activity coefficient, surface mole fraction, and partial molar area of the ith species, respectively, RT being of usual meaning. Proceeding to a one-component monolayer and setting

$$x^s = \Gamma\omega \tag{3}$$

$$\ln f^s = a(1 - \Gamma\omega)^2 \tag{4}$$

(with a as the molecular interaction constant) yielded the resultant equation[1]

$$\frac{d\Pi}{d\Gamma} = \frac{RT}{1 - \Gamma\omega} - 2aRT\Gamma\omega \tag{5}$$

where Π is surface pressure ($d\Pi = -d\gamma$).

A general theory of an equation of state for a monolayer based on the excluded area was published by the author.[2] As a response, it has been recently claimed[3] that my eq 50 is identical with above eq 5. Passing from a dimensionless to explicit form, eq 50 can be written as

$$\Pi = \int_0^\Gamma \frac{RT}{1 - \Gamma a^{ex}} d\Gamma + \Pi_l \tag{6}$$

where a^{ex} is the excluded area and Π_l is the long-range part of the surface pressure. Equation 6 is thermodynamically rigorous, and I named it the master equation since eq 6 can be used as a template for deriving two-dimensional equations of state for various models. Despite the similarity of eqs 5 and 6 in form, the rebuttal of the identity of eqs 5 and 6 is self-evident since the partial molar area ω and the excluded area a^{ex} are quite different quantities. However, the whole above derivation of eq 5 requires much more comment.

The properties of partial molar quantities are well known in thermodynamics. In particular, we have the identity

$$\sum_i \omega_i \Gamma_i = 1 \tag{7}$$

for the partial molar areas. If eq 7 is taken into account, putting eq 2 in eq 1 leads to the expression

$$d\gamma = -RT\sum_i \Gamma_i \, d \ln(f_i^s x_i^s) + d\gamma \tag{8}$$

so that $d\gamma$ (or $d\Pi$ since $d\Pi = -d\gamma$) is eliminated. This happens irrespective of whether a substrate participates or not in a monolayer. Further derivation becomes useless since no relation containing Π follows from eq 8. If, however, the thermodynamic condition expressed in eq 7 is ignored and resultant equations are written in terms of Π, all these equations are fantoms and should be meaningless. Let us illustrate this for eq 5. For a one-component monolayer, the partial molar area changes to the molar area $\omega = 1/\Gamma$, whereas eq 7 becomes

$$\omega\Gamma = 1 \tag{9}$$

Putting eq 9 in eq 5 produces infinity, which shows eq 5 to be meaningless.

Among other mistakes, the following can be noted. The partial molar area does depend on state parameters and may not be treated as a constant. Equation 3 is wrong. The product $\omega_i\Gamma_i$ is rather an area fraction, but not a mole fraction. The only common feature of $\omega_i\Gamma_i$ and x_i^s is that they simultaneously become equal to unity. But these are the details. The general conclusion follows: since eq 5 is meaningless, the same should be said about all subsequent relationships following from eq 5. The classical van der Waals, Frumkin, and Volmer equations were written incorrectly[1] (a proper form for these equations can be found in my publiction[2]), and this concerns other equations of state in the cited paper[1] and in numerous subsequent publications of the same authors in this journal.

One can reasonably ask: if the equations of state mentioned were meaningless, how could it happen that they were in agreement with experiment? The explanation is very simple. Equations 5 and 6 are of the same form. The authors, thinking that they work with eq 5, dealt, in reality, with my eq 6. Selecting a value for ω to fit experimental data, they actually selected a value for the excluded area a^{ex}. That secured a good result. Concerning a possible confusion between the partial molar area and the parking area (or the closest-packing area), it should be emphasized that this is just the partial molar area what should stand in eq 2. This follows from one of the Maxwell relationships

$$\left(\frac{\partial\mu_i}{\partial\gamma}\right)_{T,Ni} = -\left(\frac{\partial A_t}{\partial N_i}\right)_{T,\gamma,N_{j\neq i}} \equiv -\omega_i \tag{10}$$

where A_t is the total monolayer area and N_i is the total number of molecules of the ith species in the monolayer. This makes the above criticism reasonable. To conclude, one can say the approach of Fainerman and Vollhardt is too simple to be correct. If their derivation were correct, it would have been done a long time ago.

References and Notes

(1) Fainerman, V. B.; Vollhardt, D. *J. Phys. Chem.* **1999**, *103*, 145.
(2) Rusanov, A. I. *J. Chem. Phys.* **2004**, *120*, 10736.
(3) Vollhardt, D.; Fainerman, V. B.; Liu F. *J. Phys. Chem. B* **2005**, *109*, 11706.

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