PHYSICAL REVIEW A VOLUME 15, NUMBER 6 JUNE 1977

Equation of state of fatty-acid monolayers on water

Beth Stoeckly
Department of Physics, University of California, Santa Barbara, California 93106
(Received 13 September 1976)

A model is presented to explain the observed high surface compressibility and low surface prsssure in the liquid-gas critical region of fatty-acid monolayers on water. The molecules are assumed to form tightly bound clumps, and the clumps then act as the basic particles of the gas. With several assumptions, the model is reduced to a three-parameter equation of state. With parameters chosen to give correct critical temperature, area, and surface pressure, the equation approximates the remaining data only qualitatively; but it is a distinct improvement over past theories, and much of the remaining discrepancy can be attributed to the assumptions made.

I. INTRODUCTION

If a sufficiently small quantity of fatty acid is introduced at the interface between water and air, it will remain as a monolayer or submonolayer at the interface. From measurements of surface pressure as a function of area molecule, it has long been known that such films exhibit several phases and that in the limit of large area per molecule they behave like a two-dimensional ideal gas.[1] Recent experiments by Kim and Cannell[2] and by Hawkins and Benedek[3] have yielded extensive and precise data for a single substance, pentadecanoic acid, $CH_3(CH_2)_{13}COOH$ on pH-2 and distilled water substrates respectively, in the region of temperature and density around the gas-liquid critical point. These data show critical behavior resembling in a general way the behavior of three-dimensional fluids and yielding mean-field critical exponents.

However, the isotherms for the films differ in several respects from what would be expected from the study of three-dimensional fluids. Figure 1 shows the two-dimensional versions of the ideal-gas law and critical isotherms of the two standard two-parameters equations of state used to represent critical behavior (with parameters chosen to give the experimental critical temperature and area) along with the Kim and Cannell's data for their critical temperature. The data show remarkably little increase in pressure as the area is decreased. In fact, the ratio of critical surface pressure to ideal-gas surface pressure at the same temperature and area is 0.375 for Van der Waal's equation, 0.27 for Dieterici's equation, and 0.1 for Kim and Cannell's data. In addition, the experimental isotherms remain convex downward far from the coexistence region.

One explanation which has been offered[4] for these effects is that the parameters describing the excluded area and long-range attraction of the molecules are really area dependent. This is so because the molecules can change their internal configurations and orientation to the plane as the film is compressed, but it cannot account for the observed lack of pressure.

This paper proposes a model based on the idea that the molecules may form significant numbers of tightly bound dimers, trimers, etc., thereby reducing the number of free objects forming the gas. The molecules are polar, having about the same dipole moment as water molecules; therefore, a rough estimate of the binding energy available may be obtained from the heat of vaporization of water, which is 0.42 eV/molecule, or $\sim 16\, kT$. The tendency to form clumps should be greater in two dimensions than in three because the entropy cost is lower. Polymerization has been suggested[5] (perhaps not for the first time) as the reason for the lower ratios of critical pressure to ideal-gas pressure in polar gases than in nonpolar gases. However, this author is not aware of any published quantitative calculations incorporating this idea.

With several assumptions, this model gives a three-parameter equation of state. The parameters are then chosen to match the critical point of Kim and Cannell's data, and the equation gives a qualitative fit over a large region. The calculated isotherms are also concave downward over a large region. Since the model is still a mean-field model, it should have mean-field critical exponents; this is confirmed by explicit calculation of the compressibility.

II. THE CLUMP MODEL

The number of clumps of each size is found by studying the equilibrium of the sequence of reactions

$$C + C \rightleftharpoons C_2, \quad C + C_j \rightleftharpoons C_{j+1},$$

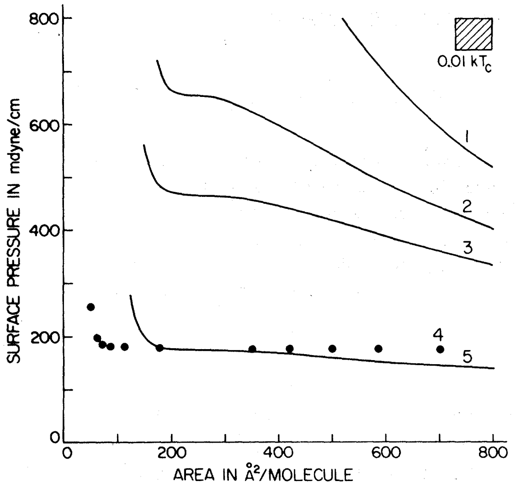

FIG. 1. Ideal-gas law (1), Van der Waal (2), and Dieterici (3) critical isotherm, Kim and Cannell critical isotherm data (4), and clump-model critical isotherm (5). Parameters in (2) and (3) are picked to match T_c and A_c; those in (5) to match T_c, A_c, and Π_c. All are plotted for 300 °K. Experimental errors are smaller than the plotting symbols; experimental values of Π are distinguishable.

where C_j represents a clump of j molecules. If N_j is the number of clumps of j molecules in the total area A, then the law of mass action adapted to two dimensions gives

$$N_1 N_j / N_{j+1} = z_1 z_j / z_{j+1}\,, \tag{2.1}$$

where z is the partition function for a clump of j molecules and is given by

$$z_j = A\,\frac{2\pi m_j kT}{h^2} \sum_i e^{-E_i/kT}\,. \tag{2.2}$$

Further analytic progress is made possible by assuming that there is a constant binding energy per molecule (D) in the clump and ignoring any change in the internal excitation energies of the molecules due to clumping. Then the sum in equation (2.2) may be approximated by $e^{+(j-1)D/kT}$.

With the definition $n_j = N_j/A$, Eq. (2.1) may be rewritten

$$\frac{n_1 n_j}{n_{j+1}} = \frac{j}{j+1}\,\frac{2\pi mkT}{h^2}\,e^{-D/kT}\,. \tag{2.3}$$

The factor $j/(j+1)$ comes from the masses; m is the mass of the monomer. n_j can be expressed in terms of n_1 and constants by taking the product of all the equations of the form (2.3) up to the jth, giving

$$n_j = n_1^j\, j r^{j-1} \tag{2.4}$$

with

$$r \equiv (h^2/2\pi mkT)e^{D/kT}\,.$$

The effective number density $\bar{\rho}$ (called the density of clumps, and including monomers) is given by

$$\bar{\rho} = \sum_{j=1}^{\infty} n_j = \sum_{j=1}^{\infty} j n_1^j r^{j-1}\,. \tag{2.5}$$

The measured number density ρ (density of molecules) is given by

$$\rho = \sum_{j=1}^{\infty} j n_j = \sum_{j=1}^{\infty} j^2 n_1^j r^{j-1}\,. \tag{2.6}$$

These sums can be evaluated easily by relating them to derivatives of the geometric sum $\sum_j (n_1 r)^j$. Eliminating n_1 between the resulting equations gives

$$n_1 r = \frac{1-\bar{\rho}/\rho}{1+\bar{\rho}/\rho} \tag{2.7}$$

and

$$\rho^2 = 4r\bar{\rho}^3 + \bar{\rho}^2\,. \tag{2.8}$$

Equation (2.7) shows that $n_1 r < 1$ always so the series converges. Equation (2.8) gives an explicit relationship between the densities of molecules and clumps.

If clumping were the only deviation from ideal behavior, the equation of state would be

$$\Pi = \bar{\rho} kT \tag{2.9}$$

where Π is the surface pressure. This equation gives lower pressures than the ideal-gas law ($\Pi = \rho kT$), but it exhibits no phase transition.

The factors responsible for the existence of a phase transition are the same as in three-dimensional fluids: there is a long-range attraction between molecules and an area excluded by the area of the molecules themselves. For simplicity, the excluded area per molecule, A_0, is assumed constant, independent of clumping. While this is probably not true, it permits the clumping idea to be studied in an equation with a phase transition without any assumptions about the structure of the clumps. The fraction of the total area which is excluded by the molecules is ρA_0, so including this effect in the equation of state gives

$$\Pi = \bar{\rho} kT/(1-\rho A_0)\,. \tag{2.10}$$

The factor $1-\rho A_0$ is a two-dimensional form of the usual excluded volume correction; it says that the effective area is the total area minus the area of the molecules themselves.

There are several ways commonly used to include the long-range attraction of the molecules. The one introduced by Dieterici[5] is most successful for describing the critical region.[6] It is reasonable to assume that the form of the long-range attraction of the molecules is unaffected by clumping. It is an average over all the positions of all the distant molecules, and the short-range part of the intermolecular potential has already been absorbed into the binding energy of the clump. The final equation of state then becomes

$$\Pi = \frac{\bar{\rho} kT}{1 - \rho A_0} e^{-\alpha\rho/kT}. \tag{2.11}$$

This equation differs from Dieterici's equation only in that it contains $\bar{\rho}$ in place of ρ; $\bar{\rho}$ is calculated from Eq. (2.8). There are three parameters in the final equation of state: D, A_0, and α. It is therefore possible to match the critical point (one data point and two vanishing derivatives) and ask (1) whether the equation then fits the rest of the data reasonably and (2) whether the necessary parameter values are physically reasonable.

To relate the critical values of Eq. (2.11) to the parameters, it is necessary to set

$$\left.\frac{\partial \Pi}{\partial A}\right|_T = 0 \text{ and } \frac{\partial^2 \Pi}{\partial A^2} = 0. \tag{2.12}$$

Explicit calculation is made possible with little loss of accuracy by assuming that in the critical region $4r\bar{\rho} \gg 1$ so that $\rho^2 \approx 4r\bar{\rho}^3$. Actually, $4r\bar{\rho}_c$ will turn out to be around 16. Then the conditions of Eq. (2.12) give

$$A_c \approx 2.22 A_0, \tag{2.13}$$

$$kT_c \approx \alpha / 3.3 A_0, \tag{2.14}$$

and D can be chosen to match Π_c. When values chosen from these equations are substituted into (2.11) using the full equation (2.8), they are found to give back T_c and A_c within 1%. This agreement is easily improved by judicious manipulating. The numbers used in the figures are

$$D = 0.354 \text{ eV}, \quad A_0 = 108 \text{ Å}^2, \quad \alpha = 9.32 \text{ eV Å}^2. \tag{2.15}$$

Kim and Cannell's data give

$$T_c = 26.27\,^\circ\text{C}, \quad \Pi_c = 174 \text{ mdyn/cm}, \quad A_c = 240 \text{ Å}^2.$$

Figure 1 shows the clump-model critical isotherm on the same scale as the other equations. Figure 2 shows calculated isotherms and Kim and Cannell's data for three temperatures. The fit is not good, but the calculated isotherms have the right qualitative features and roughly the right numbers.

No fluctuations or special critical effects have been included in the model; so the values of critical exponents obtained from it should be mean-field values. The isothermal compressibility ($K_T \equiv -A^{-1} \partial A / \partial \Pi |_T$) can be calculated directly from Eq. (2.11) by differentiation. Again, it is useful to assume $4r\bar{\rho} \gg 1$. Expanding in $(T - T_c) > 0$ at $A = A_c$, one finds straightforwardly that

$$K_T \propto 1/(T - T_c)$$

as in any other mean-field theory. Exponents below T_c cannot be calculated directly from Eq. (2.11) because, for these isotherms, the formula must be supplemented by a Maxwell equal-area construction.

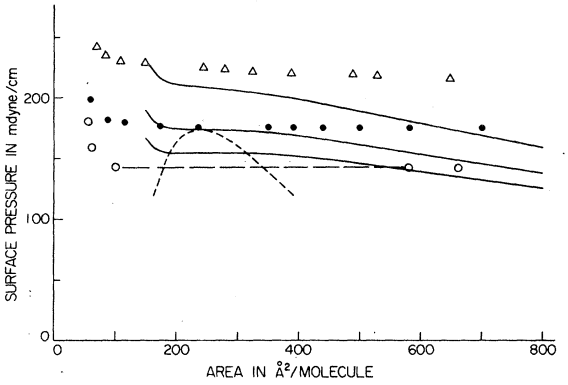

FIG. 2. Calculated isotherms and Kim and Cannell data for 34.69 °C (top), 26.77 °C (middle), and 21.96 °C (bottom). Experimental errors are smaller than the plotting symbols. The long dashed line between data points represents the observed coexistence region. The short dashed curve represents the limits of the coexistence region for the calculated isotherms.

It is interesting to see how many clumps of each size the model predicts. Equations (2.7) and (2.4) and (2.8) can be used to calculate all the n_j's for any given point. The fraction of clumps having j molecules is then

$$\bar{f}_j = n_j / \bar{\rho}.$$

Figure 3 shows $\bar{f}_j$ versus j for two different densities along the critical isotherm. It is interesting to note that as the film is compressed, the actual number density of every size clump increases monotonically while the fraction of clumps represented by small clumps decreases. Between the two histograms in Fig. 3, the density of molecules has increased by a factor of 5, the density of clumps by a factor of 3, the density of monomers by a factor of 1.3, 10-mers by a factor 26.7, and 30-mers by a factor of 2×10^5.

III. DISCUSSION

From Fig. 2 it is apparent that Eq. (2.11) (with parameters adjusted to give the experimentally

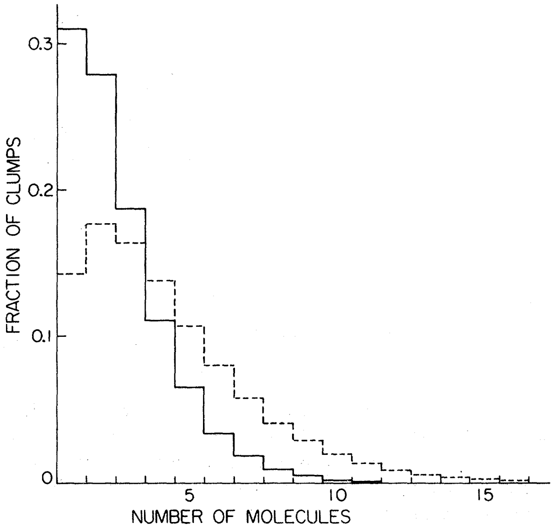

FIG. 3. Distribution of clump sizes predicted at 300 °K for $A = 200$ Å^2 (dashed) and $A = 1000$ Å^2 (solid).

observed critical point) gives $|\partial \Pi/\partial A|_T|$ too large and $\partial\Pi/\partial T|_A$ too small. The fit fails badly on the liquid side of the coexistence region. The discrepancies in the area dependence can be attributed to the two assumptions, that the binding energy per molecule in a clump and the excluded area per molecule are constants.

The choice of a constant binding energy is most serious at low densities where small clumps predominate. The molecules in different size clumps have different average numbers of nearest neighbors, and therefore, may have different binding energies per molecule. An improvement could be made by associating a binding energy with each nearest-neighbor pair instead of each molecule, but this would require some further assumption on the structure of the clumps and would yield a numerical rather than an analytic relationship between the densities of clumps and of molecules.

The discrepancies at high densities occur because the molecules do not have a constant excluded area. At low densities the molecules assume bent configurations. The energy needed to bend an alkane chain by rotating a C-C bond is only about 0.02 eV;[7] there are two bent configurations per bond and 13 C-C bonds in the alkane-chain part of the molecule. Thus the large degeneracy of configurations with one or more bends will lead to their predominance when the molecules are relatively free. Such configurations have larger cross-sectional areas than straight, erect chains. As the film is compressed, it has long been known that the molecules remain in a monolayer up to densities which could only be achieved by straight chains, erect or all tipped at the same angle, close packed in the plane. But it is not known just how the excluded area varies with density, thus any improvement in this approximation will require further assumptions. The delicacy with which such improvements must be made can be seen by noting that the shaded area in Fig. 1 represents an energy of only 0.01 kT_c.

The equation of state in its present form may be expected to fit better a film of molecules with acid groups on both ends, as such molecules have less freedom to vary their cross-sectional area.

The values of parameters needed to match the critical point are not unreasonable. The binding energy per molecule is less than, but the same order of magnitude as, the heat of vaporization of water. The excluded area of 108 Å^2 could well describe the cross-sectional area of a bent molecule. And the long-range attraction parameter is somewhat smaller but of the same order of magnitude as the parameter in the Dieterici equation of Fig. 1. This is as it should be since part of the intermolecular attraction has already been included in the binding energy.

The improvement in the fit to the data and the degree to which remaining discrepancies can be attributed to the assumptions made in deriving the explicit equation of state lead to the conclusion that the basic mechanism of clumping is probably the important effect not previously considered.

ACKNOWLEDGMENTS

The author is indebted to Dr. D. S. Cannell, Dr. M. W. Kim, Dr. D. J. Scalapino, and Dr. W. H. Weinberg for helpful discussions and encouragement, and especailly to Dr. Kim for lengthy discussions of the experimental details and for sharing his data with me.

[1] G. L. Gaines, *Insoluble Monolayers at Liquid-Gas Interfaces* (Wiley, New York, 1966).

[2] M. W. Kim and D. S. Cannell, Phys. Rev. Lett. 35, 889 (1975); Phys. Rev. A 13, 411 (1976).

[3] G. A. Hawkins and G. B. Benedek, Phys. Rev. Lett. 32, 524 (1974).

[4] M. W. Kim, Ph.D. thesis (University of California, Santa Barbara, 1975) (unpublished).

[5] C. Dieterici, Ann. Physik Chem. 69, 685 (1899).

[6] J. O. Hirschfelder, C. F. Curtiss, and R. B. Bird, *Molecular Theory of Gases and Liquids* (Wiley, New York, 1964), p. 250ff.

[7] P. F. Flory, *Statistical Mechanics of Chain Molecules* (Interscience, New York, 1969), p. 55ff.