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# The equation of state of dense fluid monolayers

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The equation of state of a two dimensional fluid of particles, interacting through a pair potential which imitates the potential between parallel carbon chains in dense monolayers, is calculated by the molecular dynamics technique and compared with monolayers of alcohols on water.

## I. INTRODUCTION

Molecules which consist of a hydrophilic and a hydrophobic part are named amphipathic molecules. Such molecules are found in biological systems where they form double layers (membranes). Monolayers and bilayers of amphipathic molecules can exist in different thermodynamic states.<sup>1,2</sup> In biological systems the states of the membranes correspond to dense fluid and solidlike states where the hydrophobic chains are close packed.

Using molecular dynamics technique<sup>3,4</sup> we have calculated the equation of state of a two dimensional dense fluid of particles, interacting through a pair potential which imitates the potential between such carbon chains. The calculations are compared with the spreading pressure of dense monolayers of alcohols on water, which are believed to be the experimental data which are closest to the model.

## II. THE MODEL

Suppose the potential energies between carbon chains may be written as a sum of pair energies between  $-\text{CH}_2$  units.<sup>5,6</sup> When the interchain distance  $r$  is short compared with the length of the chains, the London dispersion energy between two parallel carbon chains in an all-*trans* conformation varies as  $r^{-5}$ . This has led Salem to propose an energy function for the total interchain energy between such two parallel chains to be<sup>5</sup>

$$u(r) = \left( \frac{q}{5} - 1 \right) \left[ \left( \frac{r_m}{r} \right)^q - \frac{q}{5} \left( \frac{r_m}{r} \right)^5 \right], \quad (1)$$

where  $u(r_m) = -n\epsilon$  and  $q$  is an empirical power for the short range repulsive interaction between the chains. Salem proposed the power  $q$  to be equal to 25, which gives a ratio 5 to 1 between the attractive and repulsive energies at equilibrium distances, in agreement with his calculations. On the other hand, the effective (pseudo) pair potential between simple molecules in (three dimensional) liquids is known to be less repulsive than the pair potential between two isolated molecules and well described by a power 12 of the repulsive potential, twice the power of the attractive potential.<sup>3</sup> We have therefore performed the calculations for two different values of  $q$ :  $q = 10$  and 25.

The pressure  $P_{2D}$  of a two dimensional fluid of  $N$  particles at a temperature  $T$  and number density  $\rho$  and with the pair potential (1) is obtained by the molecular dynamics technique. The virial for the systems gives

$$P_{2D}^* = \rho^* T^* - \frac{\rho^*}{4N} \left\langle \sum_{i,j}^N r_{ij}^* \frac{du(r_{ij}^*)}{dr_{ij}^*} \right\rangle + \Delta P_{2D}^*, \quad (2)$$

where  $P_{2D}^*$ ,  $\rho^*$ ,  $T^*$ , and  $r^*$  are given in units of  $n\epsilon r_m^{-2}$ ,  $r_m^{-2}$ ,  $n\epsilon k^{-1}$ , and  $r_m$ , respectively and  $k$  is Boltzmann's constant. The symbol  $\langle \rangle$  means averaging over time. In the calculations the potential is set equal to zero after  $r_c (= 2.5r_m)$  and the contribution to the pressure  $\Delta P_{2D}^*$  from long range interactions distances is obtained from the virial equation

$$\Delta P_{2D}^* \simeq -\frac{\pi \rho^{*2}}{2} \int_{r_c^*}^{\infty} dr^* r^{*2} \frac{du(r^*)}{dr^*}. \quad (3)$$

For a discussion of this point see Appendix A.

In Table I is listed the equation of state data ( $\rho^*$ ,  $T^*$ ,  $P_{2D}^*$ ) for a two dimensional fluid using Eqs. (1)–(3). The calculations are for 256 particles, using periodic boundary conditions and for  $10^3$  time steps at equilibrium, both of which are found to be sufficient. The pressure is found to vary up to 0.03 reduced units for subsequent sets of  $10^3$  time steps; the temperature variations are about ten times less.

The equation of state for a two dimensional system with a simple pair potential like Eq. (1) has the same quantitative properties as the equation of state for a three dimensional system, displaying a solid state and a fluid state with a critical point.<sup>7</sup> The exact melting temperature and the coexisting solid and liquid densities are difficult to obtain by computer simulations<sup>8</sup>; the low temperature liquid points are therefore obtained from high temperature systems by cooling the system down. However, some of the equation of state data in Table I, for low temperatures and negative pressures, are certainly on the extensions of the fluid isochores behind the solid–fluid phase transition. Notice that the melting temperatures of membranes and monolayers can not directly be obtained from the melting temperatures of this model. It requires the total potential energy, and not only the sum over chain–chain potentials, to determine which of the states have the lowest free energy.

Dense monolayers of alcohols are believed to be the best experimental data to compare with the calculations, because the hydroxyl group is likely to change the water structure less than other polar head groups. The intermolecular potential energy of parallel amphipathic molecules with the carbon atoms in an all-*trans* configuration, on water, is not given completely by Eq. (1), but contains additional terms: one for the interaction of the

TABLE I. Equations of state data for a two dimensional fluid of particles with a pair potential given by Eq. 1.

$\rho^*$	$T^*$	$P_{2D}^*$
$q = 10$		
0.8	1.273	1.652
...	1.186	1.405
...	1.097	1.298
...	0.996	0.970
...	0.939	0.857
...	0.797	0.386
0.9	1.308	2.683
...	0.785	0.907
...	0.767	0.838
...	0.691	0.493
1.0	1.306	4.525
...	0.909	2.690
...	0.804	2.014
...	0.732	1.640
...	0.607	0.933
1.1	1.203	7.064
...	0.925	5.164
...	0.778	4.168
...	0.725	3.782
...	0.502	1.331
...	0.311	0.066
...	(0.195)	-1.246)
1.15	1.237	9.459
...	1.124	8.446
...	0.968	7.529
...	0.495	2.811
...	0.300	1.213
...	0.203	0.363
...	0.145	-0.135
$\rho^*$	$T^*$	$P_{2D}^*$
$q = 25$		
0.8	0.718	0.770
...	0.554	0.265
...	0.480	-0.021
0.9	0.758	1.941
...	0.510	0.558
...	0.391	-0.311
1.0	0.756	3.048
...	0.528	1.389
...	0.399	-0.177
1.05	0.757	4.130
	0.479	1.528
	0.347	0.293
	0.306	-0.222
1.1	0.780	6.949
...	0.503	3.727
...	0.192	0.777
	0.151	0.231
	0.138	0.052
	0.125	-0.140
1.11	0.508	4.797
	0.258	2.468
	0.145	0.830
	0.085	0.011
	0.064	-0.300

polar head group with a neighbor molecule  $u_{p-a}$  and one for the interaction of the amphipathic molecule with the water. With respect to the last term the axis of the chains in the dense monolayer are here assumed to re-

main perpendicular to the water surface, independent of the film density. If the water structure below the film is also independent of the density of the absorbed molecules, the alcohol-water interaction gives a density independent contribution to the free energy per particle in the monolayer and therefore no contribution to the pressure in the film.<sup>9</sup>

One way to take into account the polar head group interaction with a neighbor amphipathic molecule  $u_{p-a}(r)$  is to consider  $u_{p-a}(r)$  as a functional perturbation to  $u(r)$ .<sup>10</sup> For simple fluids like argon the structure of the fluids is determined by the strong repulsive part of the potential and a perturbation expansion in the London-van der Waals interaction potential converge rapidly. This result, transferred to this model, predicts that  $u_{p-a}(r)$  can be treated as a functional perturbation of  $u(r)$  only if the short range part of the pair potential energy of the amphipathic molecules is given by the repulsive part of the Salem potential (1); or, in other words, if the cross section of the polar head group does not exceed the cross section of the carbon chain. The first correction term in the perturbation expansion, the mean field term, is proportional to the square of the density, and the spreading pressure of the monolayer  $\pi$  is given by

$$\pi = P_{2D}^* n \epsilon r_m^{-2} + \gamma \rho^{*2} r_m^{-4}, \quad (4)$$

with a parameter  $\gamma$  which depends implicitly on the temperature and density through the radial distribution function for the amphipathic molecules in the monolayer. In practice,  $\gamma$  is independent of  $T$  and  $\rho$  in the relatively narrow temperature and density intervals considered below. The chain-chain interaction potential given by Eq. (1) is a drastic reduction of the potential  $u(r_i^*, r_j^*)$  between two molecules of  $n$  nuclei. However, in the mean field approximation also corrections to the chain-chain interaction potential (1) will lead to a correction of the pressure, which is proportional to the square of the density. Thus,  $\gamma$  in Eq. (4), treated as a parameter, can also correct for error introduced by Eq. (1). The equation of state data in Table I is given as points on the isochores, which are nearly linear in temperature over a wide temperature interval. From Eq. (4) we obtain the following relation for the slopes of the isochores:

$$\left(\frac{\partial \pi}{\partial T}\right)_\rho \approx \left(\frac{\partial P_{2D}^*}{\partial T^*}\right)_{\rho^*} k r_m^{-2}, \quad (5)$$

provided the mean field corrections do not depend on the temperature (through  $\gamma$ ). Equation (5) predicts that the slope of the experimentally obtained isochores should depend on the cross section ( $r_m$ ) but be independent of the length of the carbon chain ( $n$ ) and of the nature of the hydrophilic head group ( $\gamma$ ) (provided that the cross section of the polar head group does not exceed the cross section of the chain).

### III. EQUATION OF STATE OF DENSE MONOLAYERS

It is difficult to measure the pressure in a film accurately because  $\pi$  is very sensitive to impurities and also evaporation from the film plays an important role.<sup>1</sup> In fact, the limited experimental data for monolayers

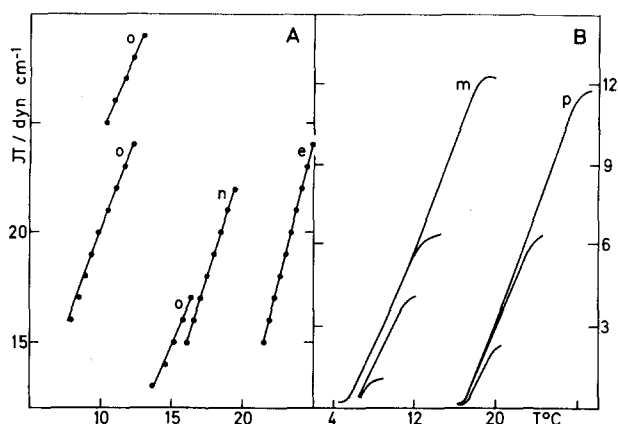


FIG. 1. The spreading pressure as a function of temperature at constant density of the monolayers. Figure 1(A) gives the spreading pressure for octadecanol (o), nonadecanol (n), and eicosanol (e) in the  $LS$  state, taken from Ref. 14. Figure 1(B) shows the spreading pressure of myristic acid (m) and pentadecylic acid (p) in the  $L_2$  state taken from Ref. 15.

of amphipathic molecules are often in mutual disagreement for those reasons. At low densities the monolayer behaves as a two dimensional ideal gas,<sup>11</sup> and even at higher densities, in the so-called extended state, the (spreading) pressure formally obeys a van der Waals equation of state for a two dimensional system<sup>12</sup> and has properties which are not three dimensional.<sup>13</sup> However, only in the highly compressed fluid and solid states of the monolayer can we hope to find the carbon chains ordered in an all-*trans* state perpendicular to the surface. The compressed fluid monolayer is often named "the liquid condensed" monolayer state ( $L_2$ ) after Adam.<sup>14</sup> At higher densities the monolayer can exist in another fluid state, the "superliquid" state ( $LS$ ) and in a solidlike state ( $S$ ).<sup>14</sup> As the density (pressure) increases the film finally collapses. The most significant difference between the two condensed fluid states is that the  $LS$  state is ten times less compressible than the  $L_2$  state.

The isochores of monolayers of different amphipathic molecules show the same qualitative picture, namely, a linear dependence of  $T$  over a wide temperature range for both  $L_2$ ,  $LS$ , and the solid state. In Figs. 1(A) and 1(B) are shown two different sets of experiments taken from Refs. 14 and 15, respectively. Figure 1(A) shows the spreading pressure for octadecanol (o), nonadecanol (n), and eicosanol (e) in the  $LS$  state and at densities  $\sim 1/20 \text{ \AA}^{-2}$ . The slopes of the lines are of the order  $2 \text{ dyn cm}^{-1} \text{ K}^{-1}$ . Figure 1(B) shows the isochores for myristic (m) and pentadecylic acid (p) in the  $L_2$  state spread on water at  $pH=2$ . The slope of the isochores are here  $\approx 1 \text{ dyn cm}^{-1} \text{ K}^{-1}$  at the highest densities  $1/30 \text{ \AA}^{-2}$  and  $\approx 0.7 \text{ dyn cm}^{-1} \text{ K}^{-1}$  at the lowest density  $1/40 \text{ \AA}^{-2}$ . From Fig. 1 can be seen that varying the number of  $-\text{CH}_2$  units in the carbon chains only results in a parallel shift in the spreading pressure in both the  $LS$  and the  $L_2$  states, as predicted by Eq. (5).

We are specially interested in the two dimensional results  $P^*$ ,  $\rho^*$ ,  $T^*$  which correspond to the dense liquid monolayers. The appropriate values of these param-

eters may be estimated as follows: The dense alcohol fluid states  $L_2$  and  $LS$  exist at areas per molecule  $A/N = 20\text{--}22 \text{ \AA}^2$  and the experiments are carried out near room temperature, where the spreading pressure varies typically from 0 up to  $\approx 30 \text{ dyn cm}^{-1}$  for alcohols with 18–20 carbon atoms. The diameter of a carbon chain in an all-*trans* state is near  $4.8 \text{ \AA}$ ,<sup>5,16</sup> and the minimum energy  $-\epsilon/k$  per  $-\text{CH}_2$  unit is calculated by Salem<sup>5</sup>, for  $q=10$  and  $q=25$  the calculations imply that  $\epsilon/k \approx 120$  and  $\epsilon/k \approx 190 \text{ K}$ , respectively. Let us furthermore assume that the hydroxyl-alcohol interaction is of the functional form given by Eq. (1) and that the strength is of the same order of magnitude as  $\epsilon$ . Using the data above the experiments correspond to the following parameters in the model:  $\rho^* = N r_m^2 / A \approx 4.8^2 / 21 = 1.1$ ,  $T^* = kT / n \approx 300 / (20 \times 120) = 0.125$  ( $q=10$ ),  $\approx 300 / (20 \times 190) = 0.08$  ( $q=25$ ) and from Eq. (4),  $P_{2D}^* = \pi \times r_m^2 / (n+1) \epsilon < 30 \times 4.8^2 / (20 \times 120) = 0.3$ , and only drastic changes in  $r_m$  and  $\epsilon$  can change these approximate values of  $P_{2D}^*$  ( $T^*$ ,  $\rho^*$ ) significantly.

We have not fitted the model to the experimental data because the data is too limited and inconsistent to do this. Instead, we have compared the model with the derivatives of the spreading pressure. The reason for this is twofold. One is that the most significant difference between the two dense fluid states is the isothermal compressibility  $\kappa = 1/\rho \times (\partial \rho / \partial \pi)_T$ , and secondly one might hope that the derivatives of the experimentally obtained pressure are less sensitive to impurities than the pressure itself (i. e., that the effects of impurities are not strongly temperature and density dependent).

The derivatives  $(\partial P_{2D}^* / \partial T^*)_{\rho^*}$  and  $(\partial \rho^* / \partial P_{2D}^*)_{T^*}$  are obtained from the equation of state data of Table I and compared with the corresponding experimentally determined values for three different alcohols, taken from Ref. 14. The results are given in Table II. The calculated values of the derivatives are obtained by setting  $r_m = 4.8 \text{ \AA}$  and are at zero pressure for  $\rho^* = 1.15$  ( $q=10$ ) and  $\rho^* = 1.11$  ( $q=25$ ), respectively. The two isochores intercept zero pressure at the reduced temperatures  $T^* = 0.16$  ( $q=10$ ) and  $T^* = 0.084$  ( $q=25$ ) and thus imitate carbon chains at low pressure with a density corresponding to  $\approx 21 \text{ \AA}^2$  and an interaction strength  $\epsilon/k \approx 100 \text{ K}$  ( $q=10$ ) and  $\approx 190 \text{ K}$  ( $q=25$ ) close to the estimated values. The slopes of the isochores  $\partial P_{2D}^* / \partial T^*$  are obtained by linear regression from the data in Table I. The isothermal compressibility of the two dimensional fluid is calculated at zero pressure using the relation  $\kappa^* = -1/\rho^* \times (\partial \rho^* / \partial T^*)_{P^*} / (\partial P_{2D}^* / \partial T^*)_{\rho^*}$ , where  $(\partial \rho^* / \partial T^*)_{P^*=0}$  is obtained from the calculated isochore lines. The uncertainty in  $\partial P_{2D}^* / \partial T^*$  is around 0.3, which corresponds to a relative uncertainty below 10%; the uncertainty in  $\kappa$  is of the same order of magnitude. As can be seen from Table II the compressibility of the two dimensional fluid is significantly less than the compressibility of the superliquid state  $LS$  and of the solid state  $S$ , which again is ten times less compressible than the liquid condensed state  $L_2$ . The derivative  $\partial P_{2D}^* / \partial T^*$  decreases with decreasing reduced density and  $\kappa^*$  increases rapidly with increasing reduced density. However, even at the low density  $\rho^* = 0.8$ , the compressibility  $\kappa$  is found to be  $\sim 0.002 \text{ cm dyn}^{-1}$ , which is still

TABLE II. The experimental data, taken from Ref. 14, is obtained in the temperature interval 7–25 °C and for film densities which correspond to from 22.6 to 19.78 Å<sup>2</sup> molecule<sup>-1</sup> or collapse. The calculated values are obtained at zero pressure at  $\rho^*=1.15$  ( $q=10$ ) and  $\rho^*=1.11$  ( $q=25$ ), respectively, and for  $r_m=4.8$  Å.

	Octadecanol	Nonadecanol	Eicosanol
$(\partial \pi / \partial T)_\rho$ (exp) (dyn cm <sup>-1</sup> K <sup>-1</sup> ) in $L_2$ state)	0.325 0.368 0.982 0.375	0.331	0.580
$(\partial \pi / \partial T)_\rho$ (exp) (dyn cm <sup>-1</sup> K <sup>-1</sup> ) in $LS$ state)	1.588 1.625 1.578	2.200	2.562
$(\partial \pi / \partial T)_\rho$ (calc) (dyn cm <sup>-1</sup> K <sup>-1</sup> )	0.5 ( $q=10$ )	0.9 ( $q=25$ )	
$\kappa$ (exp) (cm dyn <sup>-1</sup> ) in $L_2$ state)	0.0055–0.008 0.004–0.016 0.0055–0.008	0.005–0.008 0.0055–0.008 0.0047–0.008	0.004–0.009 0.004–0.016 0.004–0.009
$\kappa$ (exp) (cm dyn <sup>-1</sup> ) in $LS$ state)	0.0014–0.0017 0.0007–0.0009	0.0008–0.0009 0.0005–0.0009	0.0005–0.0009 0.0008–0.0011
$\kappa$ (exp) (cm dyn <sup>-1</sup> ) in solid state)	0.0006–0.0008	0.0007–0.0009	0.0007–0.001
$\kappa$ (calc) (cm dyn <sup>-1</sup> )	< 0.0003 ( $q=10$ ), < 0.00006 ( $q=25$ )		

significantly less than the compressibility of the  $L_2$  state at densities  $\sim 1/20$  Å<sup>2</sup> and room temperature. It is therefore not possible, even by choosing other values for  $r_m$ , for  $\epsilon/k$  to adjust both  $\partial P_{2D}^*/\partial T$  and  $\kappa$  to the experimentally obtained values.

The systematic difference between the compressibility of a fluid monolayer and of this model can be caused by several factors. The intermolecular potential (1) is drastically simplified, but on the other hand we have performed the calculations both for a “hard” and for a “soft” potential and the resulting  $\kappa_{calc}$  shows the same qualitative difference from  $\kappa_{exp}$ . We are not able to estimate the accuracy of the experimental data but believe that inaccuracy of  $\kappa_{exp}$  is not the only reason for the difference in  $\kappa_{calc}$  and  $\kappa_{exp}$ . That films in the condensed state  $L_2$  have a higher compressibility than the two dimensional fluid can easily be explained if some of the chains are not in an all-*trans* configuration in the  $L_2$  state. This is also indicated by the difference in the slopes of the experimentally obtained isochores for the two fluid states, which, according to Eq. (5), should be inversely proportional to the area of the cross sections of the chains. In the comparison between the calculated and experimentally obtained compressibility we have assumed that the potential energy for the system can be written as a sum of pair potentials of the form given by Eq. (1). However, from the expression (4) we know that corrections to this approximation should be temperature independent but strongly density dependent, and thus should show up in the compressibility.

A series of experiments could clear up the functional form and influence of the chain–chain interaction  $u(r)$  and the polar head groups interaction with a neighbor molecule  $u_{p-a}(r)$ , but unfortunately the experimental data are inadequate. Measurements of the spreading pressure

of dense monolayers of alcohols in a homologous series could test the equation of state dependence on the chain-length and experiments with molecules, with another polar headgroup such as  $-SH$  or  $-NH_2$  would show the dependence of the polar headgroup interaction  $u_{p-a}$ . A density dependent long range ordering of the sorbent below the adsorbed layer should not be possible if the amphipathic molecules are adsorbed on solid surfaces and the equation of states dependence on surface waves could be analyzed from adsorption experiments on mercury.

## APPENDIX A

The pair potential (1) between two parallel carbon chains is only asymptotically valid for interchain distances  $r$  much less than the chainlength  $L$ . The power  $-5$  of the attractive potential is obtained from the approximation

$$\tan^{-1}\left(\frac{L}{r}\right) + \frac{(L/r)}{3(1+(L/r)^2)} \approx \text{constant}. \quad (A1)$$

The left hand side approaches  $\pi/2$  for  $r \rightarrow 0$  and varies asymptotically as  $r^{-1}$  for long interchain distances. However, for the relevant distances the left hand side varies only slowly with  $r$ . Let us illustrate this by a typical example: a chain length of 25 Å and a diameter  $r_m=4.8$  Å. At the distance 4.8 Å the left side of Eq. (A1) gives 1.44 and at double the distance it is, far from being reduced to half, only reduced to 1.32.

The contribution (3) to the pressure, due to long range attractive interactions, is calculated using the potential function (1) despite the fact that Eq. (A1) in this case results in the usual London law with a total intermolecular potential which varies as  $r^{-6}$ . However, the systematic error introduced by this approximation is not

important as an example shows: the integral  $\int_{r_c}^{\infty} dr^* r^{*2} \times [du(r^*)/dr^*]$  gives  $-0.133 n\epsilon$  using Eq. (1) and for  $q=25$ , and 64% of the energy ( $-0.085 n\epsilon$ ) comes from interaction distances in the interval  $[2.5 r_m, 3.5 r_m]$ . A more correct functional form without the approximation (A1), and for a chainlength of 25 Å and a diameter of 4.8 Å, would not have given  $-0.085 n\epsilon$ , but  $-0.081 n\epsilon$ . In the previous calculations we have argued on the basis of the derivatives of the pressure. For  $(\partial P/\partial T)_\rho$  the systematic error vanishes and even for  $(\partial P/\partial \rho)_T$  it is completely negligible. Finally, we mention that Eq. (3) is obtained as usual, by approximating the radial distribution function to unity in the interval  $[r_c, \infty]$ .

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