Balance of forces in simulated bilayers.

by

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Dedicated to Professor Keith Gubbins on the occasion of his 70th birthday

Abstract

Two kinds of simulated bilayers are described and the results are reported for lateral tension and for partial contributions of intermolecular forces to it. Data for a widest possible range of areas per surfactant head, from tunnel formation through tensionless state, transition to floppy bilayer, and its disintegration, are reported and discussed. The significance of the tensionless state, is discussed.

Keywords: bilayer, lateral tension, buckling transition, tensionless.
I. Introduction: two-dimensional sheets in three dimensions.

Great interest in the properties of membranes and bilayers is reflected in the very large volume of work, reporting simulations of a variety of models and simulation methods. However, simulations including a range of areas are relatively rare and those including a widest possible range of areas - rarer still. Most papers concentrate on the "tensionless state" for which the lateral tension vanishes.

The latter is the direct counterpart of the surface (interfacial) tension between two liquids and in fact it is computed according to the same Kirkwood-Buff formula. At this stage we must mention that the physico-chemical properties of a sheet of surfactant molecules, forming a bilayer, are positively exotic. Compare with a planar interface between e.g. a liquid and its vapor or two immiscible liquids. Then the surface tension $\gamma$ is defined by

$$\left(\frac{\partial F}{\partial A}\right)_V = \gamma \quad (1.1)$$

where $F$ is the free energy, $A$ the area, $V$ the volume and the constancy of particle numbers and temperature $T$ is understood. But $\gamma$ itself is independent of the area; it is a material property, a function of state. In a shocking contrast to that, the lateral tension of a bilayer (again defined after (1.1)) is area-dependent; moreover in the same system as to composition, density, and temperature, $\gamma(A)$ can be positive or negative. Its zero defines the "tensionless state" which is of particular interest and some physical significance.

Other properties, such as internal energy $U$ or correlation functions including the structure factor $S(q)$, also display the area dependence, if a sufficiently wide interval of areas is investigated.

The peculiar shape of the bilayer isotherm i.e. of the function and plot of $\gamma(A)$, as shown and discussed in Section II, raises the question as to how it originates. A partial answer to that is provided by the split of $\gamma$ into its components.

Not all simulations are "atomistic" i.e. not all simulations construct the intermolecular total energy $E(\{r\})$ from model intermolecular potentials depending only on the spatial coordinates of the constituent particles (atoms or molecules), which energy is then used in a Monte-Carlo or Molecular Dynamics simulation scheme. One of the advantages of an atomistic simulation is the possibility of examining the role of the constituent components such as surfactant heads, solvent molecules, and surfactant tails.
This is put to use in this paper, in which we report the split of lateral tension.

Our results are reported for two kinds of simulated bilayers; these are defined in Section II.

In Section III we show the split of lateral tension into components and we discuss the physical meaning of the ”tensionless state”.

In Section IV we return to the discussion of bilayer properties and deeper distinctions between interfaces and membranes or bilayers. The discussion introduces the concept of constraint.

It also appears to be necessary to point out that a very important category of objects, called ”vesicles”, is entirely outside the realm of simulated bilayers. Merging ”membranes and vesicles” in one sentence greatly oversimplifies matters, because vesicles, like spherical micelles floating in a solvent, enclose a finite volume. The bilayers do not.

The ”widest possible range of areas” of simulated bilayer, mentioned above, refers to the limits of existence of a stable bilayer. When the imposed area is extended too much, the bilayer recedes creating a spherical hole or rather a tunnel filled with solvent joining the two sides of the solvent volume. When compressed, the bilayer flips into a ”floppy” state (see Section III) which then if compressed further, disintegrates into structureless object(s) which cannot be called a bilayer any more.

**Section II. Two kinds of bilayers.**

A planar bilayer is formed by amphiphilic surfactant molecules made each of a hydrophilic polar ”head” and hydrophobic non-polar hydrocarbon chains as ”tails”. The tails form the center of the bilayer and the two outer layers of heads separate the tails from the polar solvent (water). Therefore the cohesive energy density (CED)\(^8\) is high (solvent), high (first layer of heads), low (tails), low (second layer of tails), high (second layer of heads), high (solvent on the other side of the bilayer).

The same forces and the same preferences operate in the formation of micelles of various shapes. Normally the solvent is polar, of high CED, most commonly water, and the micelles shield their hydrocarbon tails by an outer layer of heads in contact with water. However, there exist rare examples of reverse micelles which are formed by amphiphilic molecules in a non-polar solvent of low CED. In reverse micelles, the (hydrocarbon) tails form the outward shell and the (polar) heads are in the center of
the micelle. By analogy with these I have constructed in simulations reverse bilayers which are formed in a non-polar solvent of low CED. On crossing the reverse bilayer along the z-direction perpendicular to the x-y plane of the bilayer, the sequence is now: solvent, tails, heads, heads, tails, solvent or, in terms of CED: low,low,high,high,low,low.

These cases can be and have been modelled with the use of Lennard-Jones (6-12) potential (LJ) with the minimum of 3 kinds of particles: s(solvent), h (head), t (tail). With 6 energies, 6 collision diameters, and 6 cut-off radii, various simplifications have been used in bilayer simulations with the LJ potentials.

In our work the solvent was made of structureless spherical particles; freely jointed chains of such particles of the same size have modelled the surfactant molecules making up the bilayer.

We found certain regularities in the stability of the model bilayers. We found that the chain lengths of the tails can be shortened even down to unity, the molecule becomes then a dimer (“h-t”) made of two particles. We also found that it is worthwhile to keep the presence of the solvent; in some simulations very unusual, in fact unphysical, intermolecular forces were required in order to ensure existence (in simulation) of stable bilayers made of trimers. The reverse bilayers made of trimers were successfully simulated without a solvent, although it appears this was not followed with further work. We also found that longer chains stabilize the bilayer; of the tail lengths \( l = 1, 4, 8 \) the dimers were difficult to stabilize without an extra repulsion (replacing the hydrophobic effect) from the solvent whereas, for longer chains, this extra repulsion was not necessary for stability. Chains with \( l = 8 \) produced stable bilayers with great ease.

The modelling of solvent as made of spherical structureless particles interacting with a central potential creates a certain conceptual difficulty because of the hydrophobic effect. It has been partially resolved by an introduction of an additional repulsive force between the solvent and the tails, e.g. of the form \( c/r^n \) with \( c > 0 \) and \( n=10 \) or more. A temperature dependence would be needed too, to take into account the entropic effects of the hydrophobicity.

In the case of a reverse bilayer, the reasons for its formation are mostly energetic: a pair of heads (now inside the bilayer) attract each other more strongly than any other pair and there is no hydrophobic effect since the solvent is non-polar with a weak CED.
Section III. The Lateral Tension and its Components.

A bilayer originally planar, lies in the \( x \)-\( y \) plane in the middle of a simulation box which is a parallelepiped of volume \( V = L_x \times L_y \times L_z \); its area is \( A = L_x L_y \). It is made of \( N_m \) molecules which contain \( N_m \) heads, originally \( N_m/2 \) in each of the two monolayers, so that the "area per head" \( a = A/(N_m/2) \). The bilayer is surrounded "from above" and "from below" by \( N_s \) molecules of the solvent. The overall density is \( \rho = N/V \) with \( N = N_s + (l + 1)N_m \). The lateral tension is defined\(^7\) as the response to the process of increasing the area at constant volume. With \( L_x \to L_x + \delta L_x, L_y \to L_y + \delta L_y, L_z \to L_z + \delta L_z \), the constraint of constant volume requires \( \delta L_x/L_x + \delta L_y/L_y + \delta L_z/L_z = 0 \) and the Kirkwood-Buff equation follows

\[
\gamma A = L_z(2p_{zz} - p_{xx} - p_{yy})/2
\]  

(3.1)

with the known definitions

\[
p_{\alpha\alpha} = < \sum_j r_j^\alpha \frac{\partial E}{\partial r_j^\alpha} >
\]  

(3.2)

valid for a rectangular box. The average is a canonical average at given temperature \( T \), all \( N' \)s, \( A \), and \( V \). In the simulation, for each state point of \( T, V, N_m, N_s, A \) we obtain one value of \( \gamma(A) \). In our work, \( L_x = L_y \); changing \( L_x \) to any new value, we calculate the new value of \( L_z \) needed to keep the volume \( V = L_x L_x L_z \) at exactly the same value.

Each time \( \gamma \) is computed, it is a sum of binary terms and these are grouped into partial sums so as to produce the split

\[
\gamma = \gamma_{ss} + \gamma_{sb} + \gamma_{bs} + \gamma_{bb}.
\]  

(3.3)

Here the indices \( ss \) refer to the solvent-solvent part, the indices \( sb \) and \( bs \) to the solvent-bilayer part, and \( bb \) refers to the bilayer-bilayer part. There is no approximation involved.

Fig.1 shows an example of a bilayer made of chain molecules of tail length \( l = 4 \) plus one more particle as the head, immersed in a solvent at high liquid-like density. Each \( \gamma_{\alpha\beta} \) is plotted against the area per head \( a \); the lines joining the data points are there to guide the eye, only. The contribution of solvent-solvent pairs is about 0.2-0.3 and almost constant i.e. independent of \( a \). All pairs made of solvent particle and any particle of any bilayer molecule make up the \( sb \) or \( bs \) contribution; it is also positive, varying smoothly with \( a \) and taking values between 0.5 and 1.05 . The \( bb \) contribution shows the
characteristic break into two curves, nearly linear with $a$, but one with positive slope and the other with a negative one. This pattern is transferred to the sum, eq.(3.3), total $\gamma(a)$.

Fig.2 shows the effect of size for the same chain-length $l = 4$. The solvent-solvent contribution $\gamma_{ss}(a)$ is practically independent of size, as is nearly so the solvent-bilayer part. The $bb$ part and, consequently, the total $\gamma$ display the break into two regions; the floppy part strongly affected by size and the extended region negligibly so. The bigger size shows flatter $\gamma(a)$, still negative, but closer to zero. Lowest values of $\gamma(a)$, which may be taken as the border between the floppy region and the extended region, are negative but lower value corresponds to smaller size.

These remarkable patterns are repeated for chain length $l = 8$, with breaks much more pronounced. Fig.3 shows $\gamma_{\alpha\beta}(a)$ for two sizes; the intermediate size is omitted, just as was in Fig.2, in order to make the plot clearer. Again the $ss$ part is constant and size-independent, the $sb$ part nearly so, and the total $\gamma$ along with the $sb$ part, show these remarkable features: breaks and abrupt changes of slope. For large $a$ the slope is positive and the size-dependence negligible. The transition to the floppy region occurs near $a = 1.8$ for the smaller system and the slope $d\gamma/da$ changes sign; the break is very pronounced. The transition is shifted to $a = 1.9$ in the bigger system, the break is more pronounced in the $bb$ part than in the total $\gamma$. Most characteristically in the bigger system $\gamma(a)$ is flat and near zero (though still always negative) in the floppy region. The tensionless point appears to lie on the r.h.s. curve (extended bilayer region) in this case.

All bilayer isotherms i.e. all plots of $\gamma(a)$ we have obtained$^{1-4}$ show the same pattern of two curves joined at some negative value of the lateral tension $\gamma$. We interpret the region of lower $a$ as the region of the floppy state of the bilayer which escapes into the third dimension, buckles, and takes a fuzzy and irregular form. A gently fluctuating planar bilayer is found in the other region at higher $a$’s. Generally, the region of extended bilayer includes all states with positive $\gamma$. The crossing of the isotherm with the $a$-axis marks the tensionless state. In the plots of Fig.1-3 the region of the extended bilayer has a large positive slope of $\gamma(a)$. Such positive slopes have been found independently$^{5,6}$ and also earlier$^{9-13}$. The entire range including the floppy region is found only in few references$^{2-6}$. The corresponding split of the lateral tension is found in this paper only.

The status of the tensionless state appears now in a new light, as an accidental event
resulting from the algebraic sum of positive and negative contributions after (3.3). The partial contributions suggest that the break point dividing the two branches of $\gamma(a)$ (or $\gamma_{bb}(a)$) is a truly characteristic point which ought to have a physical significance, rather than $\gamma(a_0) = 0$.

The shortest possible tail of one particle is present in a dimer. We have attempted and partially succeeded\(^1\) in simulating bilayers made of dimers, but these appeared to be only imperfectly stabilized by strong head-head and head-solvent interactions or/and the extra-repulsion introduced artificially to mimic the hydrophobic effect, as invented earlier\(^9\). Possibly at other densities and temperatures the simulations would have been more encouraging. We do not show these results. As mentioned in Section II, we turned to the new case of reverse bilayers formed in a weakly interacting solvent and succeeded in producing (in simulation) stable reverse bilayers of amphiphilic dimers\(^2\)\(^,\)\(^4\). Fig.4 and 5 show a selection of several characteristic cases, each for two sizes. These cases are: (a) extra repulsion added, (b) no extra repulsion, (c) no extra repulsion and longer range of attractive forces. In cases (a) and (b) the cut-off was the generally used $r = 2.5$, in the case (c) it was $r = 3.2$. For clarity, we split the data into two Figures: Fig.4 shows $\gamma$ total only, for all 5 systems whereas Fig.5 shows the components $ss$, $sb$, and $bb$. All curves for all 5 systems in Fig.4 show a pattern similar to $\gamma(a)$ in Fig.3 (for $l = 8$). This characteristic pattern is: almost linear rise with $a$ for larger $a$ and almost constant negative $\gamma$ for small $a$. Such a description fits bigger systems better. The biggest system of an area about $100 \times 100$ of reverse dimers case (a) is shown in Reference 4. As can be seen from Fig.4, the plot again strongly suggests a transition between two forms of the bilayer and certainly the existence of two regions\(^1\)\(^–\)\(^5\). In the floppy region $\gamma < 0$ and the bigger the system the closer to zero $\gamma$ becomes. Fig.5 shows the components of $\gamma$ but without $\gamma$ itself. The pattern is similar to those shown in Fig.1,2,3 except that the ss contribution to $\gamma$ is now negative, between -0.6 and -0.2, the sb contribution much larger, between 2. and 3.6. The $bb$ contribution is, for all sizes, practically linear in $a$ with again negative slope and negative value in the region of ”floppy” state. The transition appears softer than for chain molecules, especially those with longer tails where the breaks were sharp (see Fig.3) in small systems.

The status of the tensionless state appears to be relegated to the category of accidental coincidences. An analogy may be drawn with the equation of state of liquid in equilibrium with its saturated vapor; certainly $P = 1$ is a particular point on the vapor pressure curve, but it has no particular physical meaning - in contrast with e.g. the
triple point. The only physical consequence of zero in lateral tension is the special form of the structure factor\(^{10,1-4,5}\). However, even this has been questioned recently\(^{12,4}\). In a detailed investigation of the structure factor \(S(q)\) of a simulated bilayer, which should, for small \(q\), asymptotically vary as \(1/S \sim kq^4 + gq^2\) where \(k\) is the rigidity constant and \(g\) - the surface tension, we found \(g \geq \gamma\) systematically\(^4\). The explanation advanced elsewhere\(^{12}\) is that \(\gamma \delta A\) is not the correct work of deforming a bilayer initially planar, but \(g \delta A_{\text{true}}\) is. Here \(A_{\text{true}}\) is the true area of the interface or bilayer, obtained by following its surface, whereas \(A \equiv L_x L_y\) is the projected area. Since \(S(q)\) measures the spontaneous fluctuations, \(gq^2\) is correct and \(\gamma q^2\) is not. On the other hand, when measuring the response of the system to an imposed change in the projected area, \(\gamma \delta A\) is the correct free energy increment. The increase in the projected area is under control of the experimentalist; the change of the true area induced by the twists and bends of the bilayer, is not. By taking these arguments into account, the correct definition of the tensionless state was assumed\(^{12}\) to be \(g = 0\) and interpolation procedures were used\(^{12}\) to determine the new correct tensionless state. Whether the details of the advanced explanation\(^{12}\) are correct or not, it is obvious that \(g\) parametrizes the spectrum \(S(q)\) of spontaneous shape fluctuations. The difference between \(g\) and \(\gamma\) was also discussed elsewhere\(^{13,6,15}\). The zero of \(\gamma(a)\) is unambiguous in small systems; in large system of reverse bilayers\(^4\) it falls within the narrow region of fastest change in slope, signalling the transition of the bilayer to the floppy state. Then the precision of its determination is doubtful. Some of this ambiguity is seen in Fig.4 and in Figures of Reference 4.

**Section IV. Discussion.**

We have noted in the Introduction that, to a physical chemist familiar with the interfaces, some properties of a bilayer are truly exotic. Let us list these properties: (1) the derivative given by eq.(1.1) depends on the specific area; (2) it can be negative; (3) extension of the area leads to a hole or tunnel as the bilayer resists further extension; (4) there is distinction between actual area and the projected area but the bilayer keeps its true area nearly constant; (5) as there are two areas, there are two interfacial tensions.

Definitely this is not what we learn from classical textbooks on thermodynamics.

The feature (1) has been seen in all simulations, including these over a wide range of (projected) areas\(^1-6,9-15\). The feature (2) has also been seen\(^2-6,11,12,13,15\). The feature (3) has not only been seen\(^2,4,15\) but also investigated\(^15\). Distinction (4) has been the
subject of papers\textsuperscript{13,5} specifically devoted to it. Finally, the existence of an\textit{(other) surface tension(s)}, besides the lateral tension, has been repeatedly surmised\textsuperscript{5,6,11,13}; equations have even been derived\textsuperscript{14}.

The explanation of such specific behaviour ultimately lies with intermolecular forces and steric effects which any future theory will have to take into account. The bilayers are made of \textit{amphiphilic} molecules, each containing a hydrophilic part and a hydrophobic part (or more generally, ”solvophilic” and ”solvophobic”). These molecules use their very special setup of intermolecular forces to create a stable sheet of constant mass (and approximately constant area). This creates a new situation with a constraint of given total area almost conserved when the projected area is varied by varying the simulation box.

The constraint of constant mass (or anything related to it) is entirely absent in fluctuating interfaces. The molecular mechanism of fluctuations of shape of e.g. a liquid-vapor interface, involves diffusion from either phase; a local protrusion or excursion of the interface takes place not only by deforming the existing surface but also by absorbing or releasing molecules from/to either phase.

The surface of a perfect crystal in equilibrium with its vapor is a good example; all shape fluctuations are due to evaporation or condensation.

Such processes clearly take part in shape fluctuations of a liquid surface as well.

Hence an interface is a system open with respect to particle number. It is not so with the bilayer. Not only the solvent is virtually absent from the bilayer, but also the surfactant molecules making the bilayer never leave it. In principle the surfactant must be present in the solvent but the bilayer changes shape by changing the position of its molecules, not by exchanging them with the solvent solution. The shape fluctuations take place \textit{under the constraint} of constant number of particles, i.e. constant mass.

A constant mass is implicit in the elastic theory of solids and the links to that field have already been explored\textsuperscript{5,10}. Conversely, application of the elastic theory of solids to liquid interfaces, (the so called ”drumhead model”), is clearly not quite correct by not allowing for diffusion described above.

We discuss now the new evidence for the transition. All plots of $\gamma_{bb}(a)$ and $\gamma(a)$ show some kind of break into two branches, one corresponding to the ”floppy” bilayer. Although the word ”floppy” or ”buckling” appeared occasionally\textsuperscript{4,5}, in fact the status
of the floppy region and of the transition into that region are not very clearly established. There are suggestive analogies with the crumpling transition of solid (tethered) membranes or with coiling transitions of polymers. This would suggest it is a first-order transition. The breaks in $\gamma_{bb}(a)$ (see Section III) strongly support such a hypothesis also suggesting it is an internall reorganization of the bilayer structure, in which the solvent plays a secondary role.

Further support is found with the radius of gyration of the bilayer, shown in Fig.6; the break in slope is very clear.

Finally, the issue of the other surface tension is not fully resolved. As we discussed above in Section III, one may define two surface tensions, one coupled to the projected area and the other coupled to something else, perhaps the true area. The first one is the lateral tension and the other may be that given by the virial expression derived or rather proposed recently\textsuperscript{14} or $g$ parametrizing the structure factor $S(q)$. (See the end of Section III). These last two may be equal or may be not.

I hypothesize that $g$ may be related to that given by the Zwanzig-Triegenberg (Z-T) equation\textsuperscript{16,7} - because the latter is derived by considering a spontaneous fluctuation. Now, in simulations of liquid-vapor interface, I have determined\textsuperscript{17} the surface tension from both expressions and these two numbers were equal within 0.01 percent. Thus I have confirmed the validity of the Schofield proof\textsuperscript{7} of the equivalence. Since the (Z-T) equation is derived in a grand-canonical ensemble, $g$ can only be "related to it" as stated above; the constraint would have to be introduced.

We finally remark that the constraint appears as a most natural thing in description of polymers when the polymer string has a constant number of segments. Indeed a model one-dimensional membrane/bilayer embedded in two dimensions, is identical to a model of a polymer string on a plane.
Appendix. Details of the Model Used.

The simulations themselves were in the past and also recently based on the Verlet leap-frog algorithm with Nose-Hoover thermostat and were never shorter than half a million steps, about 0.9 million in almost all runs. The intermolecular potential energy was a sum over pairs of particles; all pairs were interacting Lennard-Jones 6-12 potentials

\[ u(r) = 4\epsilon \left( (\sigma/r)^{12} - (\sigma/r)^6 \right) \]

with different parameters \( \epsilon \) and \( \sigma \) and with different cutoffs \( r_c \). A constant \( u_0 \) may be added at will and this makes no difference to forces. \( u(r) \) has a minimum at \( r = r^* \) of depth \( u(r^*) = -\epsilon \). There are two kinds of spherical particles "a" and "b". The solvent was made of particles "a" and the amphiphilic molecules of chains "abb..b". The collision diameter \( \sigma \) was common to all pairs. The cutoff parameter was \( r_c = 2.5\sigma \) for all like pairs and \( r_c = r^* \) for unlike-pair intermolecular force. All potentials were cut-and-shifted to assure continuity of force. Molecular Dynamics algorithms use forces.

The bilayer-forming amphiphilic molecules were freely-jointed chains and each intramolecular bond was made of two LJ halves thus:

\[
\begin{align*}
    u_{\text{bond}} &= u(r) & r < r^* \\
    u_{\text{bond}} &= u(2r^* - r) & (r^* < r < 2r^*) \\
    u_{\text{bond}} &= +\infty & r > 2r^*,
\end{align*}
\]

for either "a-b" or "b-b" bond. As explained in the text, for the special case of "reverse bilayers" made of dimers, a - b, the "bb" intermolecular attractions were enhanced by making \( \epsilon_{bb} \gg \epsilon_{aa} \). Thus "b"’s became "heads" located in the center of the bilayer.
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Captions to Figures

Caption to Figure 1

The general pattern of splits of lateral tension $\gamma$ according to (3.3) is shown as plots against the area-per-head $a$; here for an intermediate size of simulated bilayer with $N_m = 1800$ molecules with tails $l=4$ segments long, with all collision diameters $\sigma$ and all energies $\epsilon$ equal, at $T = 1$, $N_s + (l + 1)N_m = 49000$, liquid density $\rho = 0.89204$. The $ss$ contribution is marked with squares, the $sb$ contribution - with stars, the $bb$ contribution - with crosses, and the sum - with black circles. All data are quoted everywhere in LJ units reduced by the energy depth $\epsilon$ and collision diameter $\sigma$. The lines are there to guide the eye.

Caption to Figure 2

The split of lateral tension $\gamma$ plotted against the area-per-head $a$ for two sizes (SM) and (B) of simulated bilayer, made of $N_m = 450$ (SM) and $N_m = 3973$ (B) molecules with tails $l=4$ segments long, with all collision diameters $\sigma$ and all energies $\epsilon$ equal, at $T = 1$, $N_s + (l + 1)N_m = 12250$ (SM) and 105134 (B), liquid-like density $\rho = 0.89204$. With the notation of eq.(3.3), the contribution $ss$ is shown with triangles (SM) and squares (B) near 0.2-0.3; $sb$ - plus signs (SM) and stars (B) near 0.5-0.7; $bb$ - open circles (SM) and crosses (B) with negative slope for small $a$ and positive slope for large $a$. The sum after (3.3), $\gamma$, is shown with thick lines, black squares (SM), and black circles (B). See text and Caption to Fig.1. Compare with Fig.3.

Caption to Figure 3

The split of lateral tension $\gamma$ plotted against the area-per-head $a$ for two sizes (SM) and (B) of simulated bilayer, made of $N_m = 450$ (SM) and $N_m = 3973$ (B) molecules with tails $l=8$ segments long, with all collision diameters $\sigma$ and all energies $\epsilon$ equal, at $T = 1$, $N = N_s + (l + 1)N_m = 14050$ (SM) and 121026 (B), density $\rho = 0.89204$. With the notation of eq.(3.3), the contribution $ss$ is shown with triangles (SM) and squares (big) near 0.2-0.3; $sb$ - with plus signs (SM) and stars (big) near 0.5-1.1; $bb$ - with open circles (SM) and crosses (big). Note the negative slope for small $a$ and positive slope for large $a$. The sum after (3.3) is shown with thick lines, black squares (SM), and black circles (big). See text. Compare with Fig.2 and note: the unique breaks in $\gamma_{sb}$, almost constant slope in the region of floppy bilayer, translated into zero slope in total $\gamma$. 

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**Caption to Figure 4**

Total lateral tension $\gamma$ of reverse bilayers made of dimer molecules plotted against area-per-head $a$ for biggest (B) or smallest (SM) size, and 3 cases: (a) extra repulsion added and head-head attraction enhanced (H-H); (b) only (H-H); (c) the cutoff of attraction is a long-range $r_c = 3.2$, not $r_c = 2.5$; otherwise (a). The other parameters are: $T = 1.9, \rho = 0.89024, N_m = 2238$ dimers, $N = N_s + 2N_m = 40000$(SM) and $N_m = 5760$ dimers, $N = N_s + 2N_m = 160000$ (B). These had areas near $36 \times 36$ and near $55 \times 55$. The points are: open squares - Ba; plus signs - SMa; black squares - Bb; crosses - SMB; stars - SMc. The lines are there to guide the eye only. The deviation of data-point at $a \sim 1.13$ (black square) is due to the tunnel (hole). see Fig.5 and text.

**Caption to Figure 5**

The split of lateral tension after (3.3) of systems shown in Fig.4. See caption to Fig.4 for parameters. Here the points are: case ”Ba” contribution $ss$ - open squares, $sb$ - black triangles, $bb$ - pentagons; case ”SMa” and $ss$ - plus signs, $sb$ - open circles, $bb$ - black triangles; case ”Bb” and $ss$ - black squares, $sb$ - open triangles, $bb$ - black pentagons; case ”SMB” and $ss$ - crosses, $sb$ - black circles, $bb$ - diamonds; case ”SMc” and $ss$ - stars, $sb$ - open triangles, $bb$ - black diamonds. All $ss$ contributions cluster near -0.5, all $sb$ are $> 2.$, and all $bb$ show two regions interpreted as floppy bilayer and extended bilayer. See text.

**Caption to Figure 6**

One example of the radius of gyration for the same bilayer whose $\gamma$ is plotted in Fig.1, also plotted against area-per-head $a$. It appears to support, along with other correlations$^{3,4}$, the hypothesis of a discontinuous transition between the extended and floppy bilayer.
