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Analytic Equation of State of a Quasi One-Dimensional Model Lipid Monolayer

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The equation of state of a quasi one-dimensional model lipid monolayer is obtained in analytic form. The method used is the Laplace transform approach leading to a homogeneous Fredholm integral equation. Two cases are studied. The first considers a purely short range repulsive potential, when we recover the results previously obtained by Gianotti *et al.* (*J. Phys. A.: Math. Gen.* **25**:2889 (1992)). The second incorporates the long range attractive Kac potential, and the equation of state is calculated in the van der Waals limit. This extends the approach originally developed by Kac *et al.* (*J. Math. Phys.* **4**:216 (1963)).

KEY WORDS: Equation-of-state; one dimensional model; surfactants; amphiphilic systems; lipid monolayer; complex fluids.

1. INTRODUCTION

Lipid monolayers exhibit surface-active properties due to their amphiphilic character. The molecules forming these layers have a hydrophilic polar head group to which one or two hydrophobic alkane chains are attached. These monolayers may be formed at a water/oil (w/o) or at a water/air (w/a) interface. In this work we are concerned with the latter.

These systems have received considerable attention recently (see, e.g., the thorough review by Kaganer *et al.* (1999)$^{(1)}$ and references therein) partly because of their rich phase behaviour, partly for their relevance in a number of important biological processes.$^{(2)}$ It has been shown experimentally$^{(1)}$ that when the monolayer is in the so-called liquid condensed phase the chains are either tilted with respect to the water surface or perpendicular

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to it. This work is concerned with a quasi one-dimensional model to study the tilt- no tilt transition in lipid monolayers at the w/a interface. We shall make clear the meaning we give to "quasi" in the next section.

There is already a vast literature of theoretical models and computer simulations of model quasi one- and two-dimensional lipid monolayers.(1) Earlier work using quasi one-dimensional models are mainly lattice models.(3–5) One exception is an earlier work coauthored by one of us(6) that presented an off-lattice analytic solution of a quasi one-dimensional model for the tilt no-tilt transition. The approach used in that work is that of the Laplace transform method.(7) That work assumed short-range repulsive nearest-neighbour interactions.

The present work extends the results of ref. 6 in two ways. First we recover the solution of that work for either short-range repulsive or attractive nearest-neighbour interactions using the Fredholm's homogeneous integral equation which yields the analytic solution to this problem. In the process we correct misprints present in Eqs. (3.4) and (3.5) of ref. 6. The second, and most important, part of this work adds the attractive Kac potential(8) to the interaction between the molecules of the model lipid monolayer. We shall show below that the equation of state is then obtained analytically in the so-called van der Waals limit. The results obtained in this work extends the one-dimensional van der Waals equation derived by Kac *et al.*(9) to a quasi one-dimensional model. We notice that this is an off-lattice model with non-nearest neighbour interactions. Strictly speaking, in the van der Waals limit, when the Kac potential becomes "infinitely weak and infinitely long range," the number of neighbours becomes infinite and the system is effectively "infinite-dimensional."(10)

2. PARTITION FUNCTION OF THE MODEL SYSTEM

We consider a system of N lipid molecules such that the head groups are modelled by hard rods of length b laying on a line segment $[0, L]$, while the alkane chains are modelled by hard tails of length a attached at one end to the centre of mass of the rods.(6) Thus the ith model molecule is described by two variables t_i and ϕ_i, where t_i is the position of the centre of mass of the rod and ϕ_i is the orientation angle of the tail with $0 < t_i < L$ and $0 < \phi_i < \phi_m$, where ϕ_m denotes a maximum inclination, the tail being perpendicular to the hard-rod when $\phi_i = \phi_m/2$. It is precisely because the description of the molecule requires two variables, rather than one, that we say the system is quasi one-dimensional.

We now assume that the molecules interact with each other through a potential energy that is the sum of two terms

$$E_{\mathrm{int}}(t_1\phi_1,\dots, t_N\phi_N) = V_{\mathrm{SR}}(t_1\phi_1,\dots, t_N\phi_N) + V_{\mathrm{K}}(t_1,\dots, t_N), \tag{1}$$

where V_{SR} denotes the sum of pairwise additive short range nearest neighbour interactions, $V(|t_{i+1}-t_i|;\, \phi_i,\, \phi_{i+1})$.(6) The second term in Eq. (1) is given by the Kac potential,

$$V_{\mathrm{K}}(t_1,\ldots,\, t_N) = -\frac{1}{2}\sum_{i=1}^{N}\;\sum_{j=1,\, i\neq j}^{N}\; \alpha \mathrm{e}^{-\gamma\, |t_i - t_j|}. \tag{2}$$

Since we assume all the molecules are identical, then $E_{\mathrm{int}}(t_1\phi_1,\ldots,\, t_N\phi_N)$ and $V_{\mathrm{SR}}(t_1\phi_1,\ldots,\, t_N\phi_N)$ are symmetric in respect of the variables, $t_i\phi_i$, $(i = 1, 2,\ldots, N)$. The symmetry property of E_{int} allows us to write the canonical partition function of the system, $Z(L, T, N)$, as an ordered integral expression, namely

$$Z(L, T, N) = \frac{1}{\Lambda^N}\int_{0\leqslant t_1\leqslant t_2\cdots\leqslant t_N\leqslant L} \mathrm{d}t_1\cdots \mathrm{d}t_N \int_0^{\phi_m} \mathrm{d}\phi_1\cdots \mathrm{d}\phi_N$$
$$\times\, \mathrm{e}^{-\beta V_{\mathrm{K}}}\Pi_{i=1}^{i=N-1}\mathrm{e}^{-\beta V(t_{i+1}-t_i;\, \phi_i,\, \phi_{i+1})}, \tag{3}$$

where T is the temperature, $\beta = 1/k_{\mathrm{B}}T$ with the Boltzmann constant k_{B}, and

$$\Lambda = \frac{2\pi\hbar^2\beta}{(mI)^{1/2}},$$

where m, I and $\hbar$ denote the mass, the moment of inertia and the Planck constant divided by 2π, respectively.

Further we model the nearest neighbour potential as in ref. 6

$$\begin{aligned} V(|t_i - t_{i+1}|;\, \phi_i,\, \phi_{i+1}) &= \infty \qquad \text{for}\quad t<0\\ &= u(t;\, \phi_i,\, \phi_{i+1}) \qquad \text{for}\quad t>0 \end{aligned} \tag{4}$$

with $t = |t_i - t_{i+1}| - b(\phi_i,\, \phi_{i+1})$ and

$$\begin{aligned} u(t;\, \phi_i,\, \phi_{i+1}) &= (1-t/b)\, w(\phi_i,\, \phi_{i+1}) \qquad \text{for}\quad t<b\\ &= 0 \qquad \text{for}\quad t>b. \end{aligned} \tag{5}$$

In Eqs. (4) and (5),

$$b(\phi_i,\, \phi_{i+1}) = b \text{ for Case A;}\quad b \text{ for Case B;}\quad b(1+\mu) \text{ for Case C,} \tag{6}$$

$$w(\phi_i,\, \phi_{i+1}) = u_1 \text{ for Case A;}\quad u_1 - \Delta_1 \text{ for Case B;}\quad u_1 - \Delta_2 \text{ for Case C,} \tag{7}$$

where Case A $=[\phi_m/2>\phi_i,\ \phi_{i+1}>\phi_m/2]$, Case C $=[\phi_m/2<\phi_i,\ \phi_{i+1}<\phi_m/2)]$ and Case B $=$[otherwise]. The parameter μ characterizes the change in the distance of closest approach, the parameters u_1, Δ_1 and Δ_2 determine the strength of the potential $u(t;\phi_i,\phi_{i+1})$; see Fig. 2 in ref. 6, but note that $u(t;\phi_i,\phi_{i+1})$ may be either repulsive or attractive depending on the sign of w.

The isothermal-isobaric partition function $Y(T,p,N)$ may be obtained from the canonical partition function via a Laplace transfrom, namely

$$Y(T,p,N)=\int_0^\infty \mathrm{d}L\,\mathrm{e}^{-sL}Z(L,T,N), \tag{8}$$

where $s\equiv\beta p$ and p is the pressure of the system.

The idea of using a Laplace transform approach to obtain the equation-of-state goes back to the work of Takahashi[11] and, later, by van Hove.[12] It was the latter who has shown that, in the thermodynamic limit, the problem of solving a Laplace transform, such as Eq. (8), becomes one of finding the largest eigenvalue of a Fredholm integral equation.

In the next section we shall obtain the equations of state, first when we restrict ourselves to short range interactions, which allow us to recover the results of ref. 6, and then using the full potential given by Eq. (1).

3. EQUATION OF STATE

3.1. Short Range Interactions

In the equation yielded by substitution of Eq. (3) with $V_K=0$ into Eq. (8),[6] introduce the following variables:[6] $\tau_1=t_1$; $\tau_{j+1}=t_{j+1}-t_j$ for $j=1,2,\ldots N-1$; $\tau_{N+1}=L-t_N$. And using the new variables and integrating over τ_1 and τ_{N+1} gives[6]

$$Y(T,p,N)=\frac{1}{\Lambda^N s^2}\int_0^{\phi_m}\mathrm{d}\phi_1\cdots\mathrm{d}\phi_N\,\Pi_{i=1}^{i=N-1}\int_0^\infty \mathrm{d}\tau_{i+1}\mathrm{e}^{-s\tau_{i+1}}\mathrm{e}^{-\beta V(\tau_{j+1};\,\phi_i,\,\phi_{i+1})}. \tag{9}$$

Now define

$$K(\phi_i,\phi_{i+1};s)=\int_0^\infty \mathrm{d}\tau\,\mathrm{e}^{-s\tau}\,\mathrm{e}^{-\beta V(\tau;\,\phi_i,\,\phi_{i+1})}, \tag{10}$$

and Eq. (9) is written as

$$Y(T,p,N)=\frac{1}{\Lambda^N s^2}\int_0^{\phi_m}\mathrm{d}\phi_1\cdots\mathrm{d}\phi_N\,\Pi_{i=1}^{i=N-1}K(\phi_i,\phi_{i+1};s). \tag{11}$$

In order to calculate Eq. (11) let us consider the Fredholm's homogenous integral-equation with the kernel $K(\phi_1, \phi_2; s)$,

$$\int_0^{\phi_m} \mathrm{d}\phi_2 \; K(\phi_1, \phi_2; s)\, \varphi_j(\phi_2) = \lambda_j(s)\, \varphi_j(\phi_1), \tag{12}$$

where $\lambda_l(s)$ and $\varphi_l(\phi)$ denote its eigenvalues and eigenfunctions, respectively. The equation of state is given in terms of the maximum eigenvalue $\lambda_{\max}(s)$ of Eq. (12) as follows(13):

$$l = -\frac{\partial}{\partial s} \log \lambda_{\max}(s), \qquad (s \equiv \beta p) \tag{13}$$

where l is the average length of the system per particle. Thus the evaluation of the equation of state is reduced to that of $\lambda_{\max}(s)$.

We substitute Eq. (4) into Eq. (10), and then use the expression for $K(\phi_1, \phi_2; s)$ in Eq. (12) to obtain the following matricial equation,

$$\begin{bmatrix} K(B) & K(A) \\ K(C) & K(B) \end{bmatrix} \begin{bmatrix} a_j \\ b_j \end{bmatrix} = \frac{2\lambda_j(s)}{\phi_m} \begin{bmatrix} a_j \\ b_j \end{bmatrix}, \tag{14}$$

where

$$K(A) = K_0(s)\, f(sb, \beta u_1); \qquad K(B) = K_0(s)\, f(sb, \beta(u_1 - \Delta_1));$$
$$K(C) = K_0(s)\, \mathrm{e}^{-sb\mu} f(sb, \beta(u_1 - \Delta_2)) \tag{15}$$

with

$$K_0(s) = \frac{\mathrm{e}^{-sb}}{s} \tag{16}$$

and

$$f(x, z) = \frac{x\mathrm{e}^{-z} - z\mathrm{e}^{-x}}{x - z}. \tag{17}$$

Note that $f(x, z) > 0$ for $x > 0$, and that $K(\mathrm{A})$, $K(\mathrm{B})$ and $K(\mathrm{C})$ are positive for s positive. Moreover, note that in Eq. (12), $\varphi_j(\phi) = a_j$ for $0 \leqslant \phi \leqslant \phi_m/2$ and $\varphi_j(\phi) = b_j$ for $\phi_m/2 \leqslant \phi \leqslant \phi_m$.

From Eq. (14), we obtain

$$\lambda_{\max}(s) = \frac{\phi_m}{2} \left[K(\mathrm{B}) + \sqrt{K(\mathrm{A})\, K(\mathrm{C})}\right] \equiv \phi_m K_0(s)\, g(sb), \tag{18}$$

where

$$g(sb) \equiv g(sb; u_1, \varDelta_1, \varDelta_2, \mu)$$
$$= \tfrac{1}{2}\,[f(sb, \beta(u_1 - \varDelta_1)) + \mathrm{e}^{-sb\mu/2}\sqrt{f(sb, \beta u_1)\, f(sb, \beta(u_1 - \varDelta_2)}]. \qquad (19)$$

In Eq. (18), $K_0(s)$ and $g(sb)$ are the contributions from the hard-rod and the tail potentials, respectively. Replacing Eq. (18) into Eq. (13) and using Eq. (16) we obtain

$$l^* = \frac{1}{p^*} + 1 - \frac{\partial}{\partial p^*} \log g(p^*), \qquad (20)$$

where $l^* = l/b$ and $p^* = sb$. This equation agrees with that obtained in ref. 6 if account is taken of a misprint in their Eq. (3.5) (the term $-\frac{1}{\beta(pb-u_1)}$ inside the brackets on the rhs of their Eq. (3.5)) and a replacement in their Eq. (3.4) ($F_{ij} \to F_{i\bar{j}}$, $\bar{j}$ being not j).

3.2. Long Range Interactions: The Kac Potential

We now turn to the potential energy given by Eq. (1), with V_{K}, the Kac potential, given by Eq. (2). On account of V_{K}, E_{int} is not a potential energy of the nearest neighbour type and the method used in the preceding section cannot be applied to the present case. Instead we follow Kac *et al.*[9] by noting that the Boltzmann factor of V_{K} satisfies the identity

$$\mathrm{e}^{-\beta V_{\mathrm{K}}} = \mathrm{e}^{-N\nu/2} \int_{-\infty}^{\infty} \mathrm{d}x_1 \cdots \mathrm{d}x_N \; \mathrm{e}^{\sqrt{\nu}\,\Sigma_{j=1}^{N} x_j} W(x_1)\, \varPi_{j=1}^{j=N-1} P(x_j \mid x_{j+1}, |t_{j+1} - t_j|),$$

where $\nu = \beta\alpha$, $W(x) = \mathrm{e}^{-x^2/2}/\sqrt{2\pi}$, and

$$P(x_1 \mid x_2, t) = \frac{1}{\sqrt{2\pi(1 - \mathrm{e}^{-2\gamma t})}} \exp\left(-\frac{(x_2 - x_1 \mathrm{e}^{-\gamma t})^2}{2(1 - \mathrm{e}^{-2\gamma t})} \right) \quad \text{for} \quad t > 0. \qquad (21)$$

The substitution of the identity above into Eq. (3) gives

$$Z(L, T, N) = \frac{\mathrm{e}^{-\frac{N\nu}{2}}}{\varLambda^N} \int_0^{\phi_m} \mathrm{d}\phi_1 \cdots \mathrm{d}\phi_N \int_{-\infty}^{\infty} \mathrm{d}x_1 \cdots \mathrm{d}x_N$$
$$\times \mathrm{e}^{\sqrt{\nu}\,\Sigma_{j=1}^{N} x_j} W(x_1) \int_{0 \leqslant t_1 \leqslant t_2 \cdots \leqslant t_N \leqslant L} \mathrm{d}t_1 \cdots \mathrm{d}t_N$$
$$\times \varPi_{i=1}^{i=N-1} \mathrm{e}^{-\beta V(t_{i+1} - t_i;\, \phi_i, \phi_{i+1})} P(x_i \mid x_{i+1}, t_{i+1} - t_i). \qquad (22)$$

Thus, at the price of introducing N additional variables of integration ($x_1,\ldots, x_N$) the partition function has become a product of nearest neigbour functions.

We can now proceed as in the preceding section. By defining

$$K(x_1, \phi_1; x_2, \phi_2; s) \\ = \int_0^\infty \mathrm{d}\tau \, \mathrm{e}^{-s\tau} \mathrm{e}^{-\beta V(\tau;\, \phi_1,\, \phi_2)} \mathrm{e}^{\sqrt{\nu}\,(x_1+x_2)/2} \sqrt{\frac{W(x_1)}{W(x_2)}} \; P(x_1 \mid x_2, \tau), \tag{23}$$

we write the isothermal-isobaric partition function as

$$Y(T, p, N) = \frac{\mathrm{e}^{-\frac{N\nu}{2}}}{\Lambda^N s^2} \int_0^{\phi_m} \mathrm{d}\phi_1 \cdots \mathrm{d}\phi_N \int_{-\infty}^{\infty} \mathrm{d}x_1 \cdots \mathrm{d}x_N \, \mathrm{e}^{\sqrt{\nu}\,(x_1+x_N)/2} \\ \times \sqrt{W(x_1)\, W(x_N)}\; \Pi_{i=1}^{i=N-1} K(x_i, \phi_i; x_{i+1}, \phi_{i+1}; s). \tag{24}$$

To calculate Eq. (24) we introduce the Fredholm's homogeneous integral equation with the kernel $K(x_1, \phi_1; x_2, \phi_2; s)$ given by Eq. (23)

$$\int_{-\infty}^{\infty} \mathrm{d}x_2 \int_0^{\phi_m} \mathrm{d}\phi_2 \, K(x_1, \phi_1; x_2, \phi_2; s)\, \varphi(x_2, \phi_2) = \tilde{\lambda}(s)\, \varphi(x_1, \phi_1). \tag{25}$$

We note that this equation is a function of three rather than the two variables used in the true one-dimensional problem studied by Kac *et al.*(9) The equation of state is given in terms of the maximum eigenvalue $\tilde{\lambda}_{\max}(s)$ of Eq. (25) as follows in ref. 13:

$$l = -\frac{\partial}{\partial s} \log \tilde{\lambda}_{\max}(s), \qquad (s \equiv \beta p). \tag{26}$$

The calculation of the equation of state is reduced to that of a maximum eigenvalue. To obtain the maximum eigenvalue, we have to solve Eq. (25). However, this is only amenable to an analytic solution in the so-called van der Waals limit, $\alpha \equiv \alpha_0 \gamma$, $\gamma \to 0$. In this limit, Eq. (25) is reduced to Eq. (12). This we discuss below.

Following Kac *et al.*,(9) let us introduce the following transformation of variables

$$x_1 \equiv x + \eta \sqrt{2/\gamma}, \qquad x_2 = y + \eta \sqrt{2/\gamma}, \tag{27}$$

where η is a parameter to be chosen later in such a way that the maximum eigenvalue is the absolute maximumin in the van der Waals limit. From Eqs. (21) and (27) we obtain

$$\begin{aligned}
&\mathrm{e}^{\sqrt{\nu_0\gamma}\,(x_1+x_2)/2}\sqrt{\frac{W(x_1)}{W(x_2)}}\;P(x_1\,|\,x_2,\tau)\\
&\quad=\mathrm{e}^{\sqrt{\nu_0\gamma}\,(x+y)/2}\sqrt{\frac{W(x)}{W(y)}}\;P(x\,|\,y,\tau)\\
&\quad\times\exp\left(\eta\sqrt{2\nu_0}-\frac{\eta^2}{\gamma}\tanh\left(\frac{\gamma\tau}{2}\right)-\frac{\eta}{2}\sqrt{\frac{2}{\gamma}}\;(x+y)\tanh\left(\frac{\gamma\tau}{2}\right)\right),
\end{aligned}\tag{28}$$

where $\nu\equiv\nu_0\gamma$. Now note that

$$\lim_{\gamma\to 0} P(x\,|\,y,\tau)=\delta(x-y),\qquad \lim_{\gamma\to 0}\tanh\left(\frac{\gamma\tau}{2}\right)=\frac{\gamma\tau}{2}.\tag{29}$$

Substituting Eq. (28) into Eq. (23) and using Eq. (29), we obtain

$$\lim_{\gamma\to 0} K(x_1\phi_1;\, x_2,\, \phi_2;\, s)=\delta(x_1-x_2)\,\mathrm{e}^{\eta\sqrt{2\nu_0}}K(\phi_1,\,\phi_2;\,\tilde{s}),\tag{30}$$

where $\tilde{s}=s+\frac{1}{2}\eta^2$ and $K(\phi_1,\,\phi_2;\,\tilde{s})$ is defined by Eq. (10).

Substituting Eq. (30) into Eq. (24) and integrating in respect to $x_1,\ldots,\,x_N$ yield

$$Y(T,\,p,\,N)=\frac{\mathrm{e}^{-N\nu/2}}{\Lambda^N s^2}\int_0^{\phi_m}\mathrm{d}\phi_1\cdots\mathrm{d}\phi_N\,\Pi_{i=1}^{i=N-1}K(\phi_i,\,\phi_{i+1};\,\tilde{s})\,\mathrm{e}^{\eta\sqrt{2\nu_0}}.\tag{31}$$

On comparing Eq. (31) with Eq. (11), it is clear that the ensuring discussion to obtain the equation of state parallels that of the preceding section. Whence, the maximum eigenvalue in the van der Waals limit is obtained as

$$\tilde{\lambda}_{\max}(s)=\max_{(\eta)}\;F(\eta),\tag{32}$$

where

$$F(\eta)=\phi_m K_0(\tilde{s};\,\eta)\,g(\tilde{s}b),\tag{33}$$

with $g(\tilde{s}b)$ defined by Eq. (19) and

$$K_0(\tilde{s};\eta) = \mathrm{e}^{\eta\sqrt{2v_0}}\,\frac{\mathrm{e}^{-\tilde{s}b}}{\tilde{s}}. \tag{34}$$

In Eq. (32), $\max_{(\eta)}$ means that we choose the value of η so as to make $F(\eta)$ an absolute maximum, namely the value of η is obtained from

$$\frac{\partial}{\partial\eta}F(\eta) = 0, \tag{35}$$

which gives

$$f_s(\eta) = \sqrt{2v_0}, \tag{36}$$

where

$$f_s(\eta) = \left(1 + \frac{1}{\tilde{s}b} - \frac{\partial}{\partial\tilde{s}\,b}\log g(\tilde{s}b)\right) b\eta. \tag{37}$$

The equation of state in the van der Waals limit becomes

$$l^* = 1 + \frac{1}{\tilde{p}^*} - \frac{\partial}{\partial\tilde{p}^*}\log g(\tilde{p}^*) \tag{38}$$

with

$$\tilde{p}^* = p^* + \frac{b}{2}\,\eta(s)^2, \tag{39}$$

where $\eta(s)$ is the solution of Eq. (36) corresponding to the absolute maximum of $F(\eta)$. Or, with the use of Eqs. (36) amd (37) l^* can be expressed as

$$l^* = \frac{\sqrt{2v_0}}{b\eta(s)}. \tag{40}$$

Equations (38) or (40) is the sought analytic form of the equation of state. It agrees with the result of Kac *et al.*(9) when the hard tails contribution is ignored. Note that, in order to establish a correspondence between this work and that of Kac *et al.*(9) we have deliberately adopted a similar notation.

Given that our result recovers that of Kac *et al.*, we anticipate, though we can not prove it, that in agreement with the rigorous results of Lebowitz and Penrose,(14) our equation of state exhibits at least one phase transition and one critical point. At present, the only demonstration we can think of this result is to analyze our equation of state graphically through the behaviours of $f_s(\eta)$ and $F(\eta)$.

Note that Eq. (38) is obtained from Eq. (20) with the replacement of p^* in Eq. (20) by $\tilde{p}^*$. From Eqs. (18) and (32) the Helmholtz free energy density $a(p^*)$ is also obtained:

$$a(p^*) = a^0(\tilde{p}^*) - \frac{1}{2\beta}\eta(s)^2, \tag{41}$$

where a^0 is the free energy density function of the system with no Kac potential. It is not difficult to show that this effect of the Kac potential in the van der Waals limit is the one proved more generally by Lebowitz and Penrose:(14) Eqs. (39) and (40) shows that the replacement above is just the one of Lebowitz and Penrose.(14)

4. CONCLUSIONS

We have obtained analytical expressions for the equation of state of model lipid monolayers assuming either purely repulsive or repulsive plus attractive interactions.

The former case was discussed in an earlier work by Gianotti *et al.*(6) However, their result has misprints. If we allow for misprints in Eqs. (3.4) and (3.5) of ref. 6, their result is esseentially correct.

For the latter we have extended the approach originally discussed in the work of Kac *et al.*(9) to our quasi-one dimensional system. In practice this has meant having to deal with three, rather than two, independent variables. We have shown that in this case it is also possible to obtain an analytic solution for the equation of state in the van der Waals limit.

The kernels defined by Eqs. (10) and (23) are not symmetric due to the hard tail interaction, but we can find an appropriate coordinate system for the orientational angle of the tail making the kernels symmetric. In the present case, we used the non-symmetric kernels since the both results obtained are same and the use gives the result even directly. However, we believe that the most general treatment does require symmetric kernels.

In the present work only the heads are subjected to attractive interactions. We expect that this system will exhibit at least one phase transition and critical point that may be associated to the tilt no-tilt transition present in real monolayers. We are currently studying the possibility of obtaining analytic equations of state when attractive forces between the tails are also introduced in our formalism. However, the angular dependence of these forces introduce extra degrees of difficulty to the problem that we are trying to overcome.

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