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# Entropy Loss Induced by the Non-Crossing Nature in Multilayer-Membrane System

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We consider the non-crossing effect of the multilayer membrane system consisting of bilayer lipid sheets embedded in water. Using a simple one-dimensional model, we evaluate the free energy increment due to the entropy loss induced by the non-crossing nature. The free energy increment $\Delta f(\rho)$ per unit length of one membrane is expressed as $\Delta f(\rho) = B\rho^{2/3}$, where $\rho$ is the membrane density and $B$ is a positive constant. This anomalous behavior with the exponent 2/3 was verified by a Monte-Carlo simulation based on a solid-on-solid model.
Key words: multilayer membrane, non-crossing nature, entropy loss, self-consistent harmonic approximation, Monte-Carlo simulation

## 1. INTRODUCTION

As shown by Helfrich, fluctuation properties of the fluid bilayer lipid membrane are determined by the curvature elastic energy.[1,2] For an isolated membrane sheet, the curvature elastic energy is expressed by

$$H = \int dxdy \frac{1}{2} K |\nabla^2 u(x,y)|^2, \tag{1}$$

where the $x$-$y$ plane is chosen to be parallel to the mean membrane plane, $u(x,y)$ is the displacement of the membrane from the mean membrane plane and $K$ is the rigidity of the membrane. For multilayer membrane systems consisting of equally spaced membranes embedded in water, the non-crossing nature between the membranes decreases the fluctuations. The reduction of the fluctuations induces the entropy-loss; from the view point of the free energy, this increases the free energy.

In the present article, by a one-dimensional membrane model we analyze the non-crossing effect on the membrane density dependence of the free energy. As the Hamiltonian for an isolated one-dimensional membrane, we choose a one- dimensional version of (1):

$$H_{\rm one}(\{u(x)\}) = \int dx \frac{1}{2} K |\frac{d^2 u(x)}{dx^2}|^2, \tag{2}$$

where the shape of the membrane is denoted by $y = u(x)$. For the multilayer membrane system with the membrane density $\rho$, the free energy $f(\rho)$ per unit length of one membrane may increase with respect to that for an isolated membrane;

$$f(\rho) = f_0 + \Delta f(\rho), \tag{3}$$

where $f_0$ is the free energy of an isolated membrane and $\Delta f(\rho)$ shows the increment of the free energy induced by the non-crossing nature. According to the ordinary Landau theory, in the small membrane density limit, the additional term $\Delta f$ is expected to behave as

$$\Delta f(\rho) = c_1 \rho + c_2 \rho^2 + \cdots, \tag{4}$$

where $c_1$ and $c_2$ are constants. However, it has been well known that the Landau theory is incorrect for strongly-fluctuating systems such as the membrane systems. Nattermann[3] has proposed a simple self-consistent harmonic approximation to analyze the commensurate-incommensurate system, which is one of the strongly fluctuating systems. The critical behavior obtained by the approximation is same as that by the exact solvable models.[4,5] This shows the validity of this approximation for the strongly-fluctuation systems.

We use Nattermann's approximation and have the "anomalous" low membrane-density behavior quite different from the Landau theory:

$$\Delta f(\rho) = B\rho^{2/3}, \tag{5}$$

where$B$ is a positive constant. Thus, the free energy is no longer analytic at the point $\rho = 0$. This type of result can never obtained by the Landau theory.

To verify the above anomalous behavior, the Monte-Carlo simulation was performed. The Monte Carlo simulation strongly supports the result (5).

## 2. SELF-CONSISTENT HARMONIC APPROXIMATION

Let the multilayer membrane system consisting of $n$ one-dimensional membranes in the $L \times M$ space be considered. The shape of the $j$-th membrane is denoted by $y = u_j(x)$. The membrane density $\rho$ is given by $\rho = n/M$. As the interaction between the membranes, only the non-crossing

nature is taken into account. The partition function of the system is given by

$$Z = \int \prod_j \prod_x du_j(x)\theta(u_1 < u_2 < \cdots < u_n) \times \exp[-\beta \sum_{j=1}^{n} H_{\rm one}(\{u_j(x)\})], \quad (6)$$

where $\beta = 1/(k_{\rm B}T)$ ($k_{\rm B}$: Boltzmann constant, $T$: temperature) and $\theta$ denotes the non-crossing nature; $\theta = 1$ if $u_1(x) < u_2(x) < \cdots < u_n(x)$ for all $x$ and otherwise $\theta = 0$.

In the self-consistent harmonic approximation, a harmonic well potential is introduced instead of the non-crossing condition $\theta$. Let us introduce the variable $y_j(x)$ expressing the deviation of the j-th membrane from the reference position $j/\rho$; $y_j(x) = u_j(x) - j/\rho$. The harmonic potential expressing the non-crossing nature is given by $(1/2)m^2 y_j^2$, where $m^2$ is a positive parameter which expresses the "magnitude" of the well and is determined self-consistently. Thus, the effective Hamiltonian for the $j$-th membrane is given by

$$H_{\rm one}^{\rm eff}(\{y_j(x)\}) = \int dx[\frac{1}{2}K|\frac{d^2y_j(x)}{dx^2}|^2 + \frac{1}{2}m^2 y_j^2(x)]. \quad (7)$$

In terms of (7), the partition function (6) is approximated as

$$Z_{\rm app} = \int \prod_j \prod_x dy_j(x) \times \exp[-\beta \sum_{j=1}^{n} H_{\rm one}(\{y_j(x)\})]. \quad (8)$$

The self-consistent equation determining the parameter $m^2$ is given by

$$< y_j^2 >_{\rm eff} = C(\frac{1}{\rho})^2, \quad (9)$$

where $< \cdots >_{\rm eff}$ stands for the thermal average with respect to the "effective Hamiltonian" $H_{\rm one}^{\rm eff}$ and $C$ is a positive numerical factor. The l.h.s of eq.(9) is easily calculated and given by

$$< y_j^2 >_{\rm eff} = \frac{1}{2\sqrt{2}\beta} m^{-3/2} K^{-1/4}. \quad (10)$$

Thus we have

$$m^2 = C_1 \rho^{8/3}, \quad (11)$$

with

$$C_1 = (\frac{C}{2\sqrt{2}})^{-4/3} (k_{\rm B}T)^{4/3} K^{-1/3}. \quad (12)$$

From the partition function $Z_{\rm app}$, the approximated free energy per unit length of one membrane is given by

$$f_{\rm app} = -k_{\rm B}T \frac{1}{nL} \ln Z_{\rm app} = k_{\rm B}T[\frac{\Lambda}{2\pi} \ln \frac{\beta K}{2\pi} + \frac{\Lambda}{2\pi} \ln(\Lambda^4 + \frac{m^2}{K}) - \frac{2}{\pi}\Lambda + \frac{1}{\sqrt{2}} m^{1/2} K^{-1/4}], \quad (13)$$

where $\Lambda = 2\pi/a$ ($a$ is an atomic-scale length) is the large wave-number cut-off. Using (11), we have the free energy for small $\rho$:

$$f_{\rm app} = f_0 + \Delta f(\rho), \quad (14)$$

where

$$f_0 \simeq k_{\rm B}T \frac{\Lambda}{2\pi} \ln \frac{\beta K \Lambda^4}{2\pi}, \quad (15)$$

and

$$\Delta f(\rho) = B\rho^{2/3}, \quad (16)$$

with

$$B = \frac{1}{\sqrt{2}} \left(\frac{2\sqrt{2}}{C}\right)^{1/3} (k_{\rm B}T)^{4/3} K^{-1/3}. \quad (17)$$

In the above, $f_0$ is the free energy of an isolated membrane and $\Delta f(\rho)$ is the increment of the free energy induced by the non-crossing nature.

## 3. MONTE-CARLO SIMULATION

The anomalous small $\rho$ behavior (16) was confirmed by a Monte-Carlo(MC) simulation. A simple solid-on-solid membrane model was chosen. In the model, the membranes sit on a $\tilde{L} \times \tilde{M}$ square lattice and the shape of the $j$-th membrane is given by $(X, \tilde{u}_j(X))$, where $X$ and $\tilde{u}_j(X)$ are integer. The mean membrane running direction is chosen to be parallel to the $x$ axis. In the $x$ and the $y$ directions, the periodic boundary condition is imposed. The energy of the $j$-th membrane is given by

$$E_j = \frac{1}{2}J \sum_{X=1}^{M} [\tilde{u}_j(X-1) + \tilde{u}_j(X+1) - 2\tilde{u}_j(X)]^2, \quad (18)$$

where $J$ is the "microscopic" rigidity. The above model is a discretized version of the continuum model (2). The equivalence between (2) and (18) in the large wave-length has been shown.[6] Therefore, we can expect to obtain correct results by the Monte-Carlo analysis based on the "microscopic" model (18).

Since calculation of the free energy by means of the MC method is difficult, the internal energy $\varepsilon(\rho)$ per unit length of one membrane was calculated. The free energy and the internal energy are

related as $-T^2\partial(f(\rho)/T)\partial T = \varepsilon(\rho)$. Thus, if the result (16) is correct, the internal energy should behave as

$$\varepsilon(\rho) = \varepsilon_0 + B'\rho^{2/3}, \tag{19}$$

where $\varepsilon_0$ is the internal energy of an isolated membrane and $B'$ is a constant.

The MC simulation was performed by the energy (18) under the non-crossing condition $\tilde{u}_1 < \tilde{u}_2 < \cdots < \tilde{u}_n$. The temperature was chosen as $T = J/(2k_B)$. For thermalization, $5 \times 10^6$ Monte-Carlo steps (MCS) were required. The averages were taken over $5 \times 10^6$ MCS. The number of the membrane $n$ was taken to be 100. The length of the membrane $\tilde{L}$ was chosen as $\tilde{L} = 300 \sim 1500$ depending on the membrane density.

The $(b\rho)^{2/3}$-$b\varepsilon/(J/2)$ plot obtained by the MC simulation is shown in Fig.1, where $b$ is the lattice spacing of the solid-on-solid model. The plot sits on a straight line expressed by $b\varepsilon/(J/2) = 0.5022 - 0.2151(b\rho)^{2/3}$ in the small $\rho$ region. The slope and the intercept of the line were obtained by the least squares method. The asymptotic linear behavior of the $(b\rho)^{2/3}$-$b\varepsilon/(J/2)$ plot strongly supports eq.(19).

The $(b\rho)$-$b\varepsilon/(J/2)$ plot is shown in Fig.2. In the figure, the solid line corresponds to the asymptotic line in Fig.1. Figure 2 clearly shows the non-analytic properties of the internal energy at $\rho = 0$; it is found that the Landau approach (4) is unapplicable to the membrane problem.

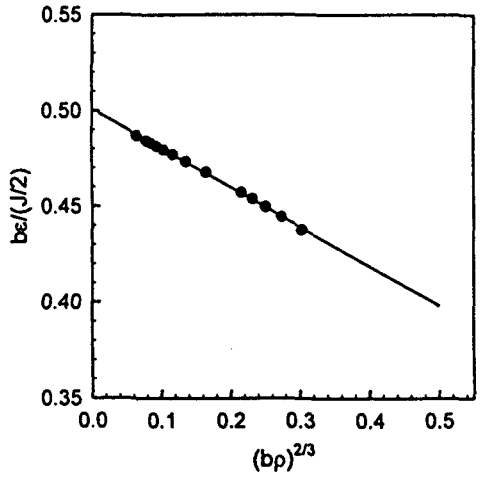


Fig.1 The $(b\rho)^{2/3}$-$b\varepsilon/(J/2)$ plot of the MC result.

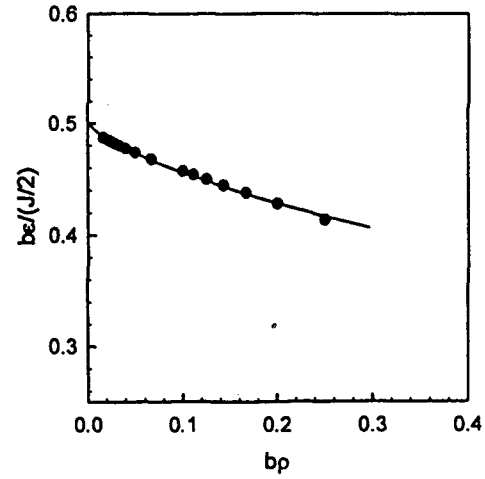


Fig.2 The $(b\rho)$-$b\varepsilon/(J/2)$ plot of the MC result.

## 4.SUMMARY

We have discussed the non-crossing nature of a one-dimensional multilayer membrane system. We have paid attention to the free energy increment due to the entropy loss induced by the non-crossing nature. By the self-consistent harmonic approximation, an anomalous behavior of the free energy $f(\rho) = f_0 + B\rho^{2/3}$ for low membrane density $\rho$ is obtained. This free energy is quite different from that obtained by the ordinal Landau theory. The free energy behavior was verified by a Monte-Carlo simulation based on the solid-on-solid model. This shows that ordinal mean-field approaches such as the Landau theory are not suitable for this membrane problem.

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