Modes of counterion density-fluctuations and counterion-mediated attractions
between like-charged fluid membranes

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Counterion-mediated attractions between like-charged fluid membranes are long-ranged and non-pairwise additive at high temperatures. At zero temperature, however, they are pairwise additive and decay exponentially with the membrane separation. Here we show that the nature of these attractions is determined by the dominant modes of fluctuations in the density of counterions. While the non-pairwise additive interactions arise from long-wavelength fluctuations and vanish at zero temperature, the short-ranged pairwise additive interactions arise from short-wavelength fluctuations and are stronger at low temperatures.

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Counterion-mediated attractions play a significant role in many physical and biological phenomena [1–10]. These attractions are responsible for fitting DNA inside a small biological container such as a viral capsid or a nuclear envelope [11] and can also be crucial in promoting adhesion and fusion of biological membranes [12]. Accordingly, significant effort has been expended in developing a practical way of investigating the nature of these counterion-mediated attractions. Besides an integral equation method [13], there have emerged two distinct approaches. The first approach [14,15], based on a charge fluctuation picture, suggests that these attractions are mediated by correlated fluctuations of ion clouds of counterions. This approach is consistent with our conception of counterions as fluctuating objects and thus merits significant consideration [16–20]. In the second approach, based on a zero temperature picture [16–20], the appearance of attractions between like-charged molecules is attributed to the strong charge correlations that drive the systems, together with counterions, into an ionic crystal. At first glance these two approaches appear to be contradictory to one another, but there is an evidence that they can, in fact, be complimentary [21–23]. Despite this, there still remain fundamental discrepancies between the two that have yet to be resolved. For the case of two planar surfaces a distance \( h \) apart, the zero-temperature picture leads to an attractive force that decays exponentially with \( h \) [16]. In the charge-fluctuation approach, however, the attractive force decays algebraically as \( h^{-3/2} \), as long as \( h \) is sufficiently large. Most recently, the apparent discrepancy between these two approaches has been examined [23] by Lau et al. Lau et al. have shown that the zero-temperature quantum fluctuations give rise to a long-ranged attraction which varies as \( h^{-7/2} \). Their theory, however, does not explain the crossover between the long-ranged interactions driven by thermal fluctuations and the exponentially-decaying interactions expected at low temperature. At finite temperatures, the long-ranged interactions supported by the charge-fluctuation approach should exist and constitute a dominant contribution to the plate-plate interactions. Furthermore, when applied to many rod systems [2,22–23], the charge-fluctuation approach suggests that interactions between rods are not pairwise additive while the exponentially decaying interactions between plates as implied by the zero-temperature approaches are pairwise additive.

In this Letter, we present a simple theoretical approach to counterion-mediated interactions between fluid membranes in order to bridge the gap between the two existing theories. In particular, we show that the nature of these attractions is controlled by the dominant modes of fluctuations in the density of counterions. At high temperature, the membrane interactions are dominated by long-wavelength fluctuations in the counterion density, i.e., fluctuations at large length scales. The resulting long-wavelength interactions are shown to be long-ranged and non-pairwise additive. As the temperature decreases, the high-temperature behavior of the membrane interactions crosses over to the behavior expected at low temperatures. At low temperatures, the membrane interactions are mainly determined by the short-wavelength charge fluctuations. We find that the resulting interactions decay exponentially with the separation between the membranes and are approximately pairwise additive. Finally, we obtain a phase diagram to depict the two distinctive regimes characterized by the corresponding dominant modes, and the crossover boundaries between the two.

The system we consider here consists of negatively charged parallel membranes surrounded by neutralizing counterions of opposite charge. In the following derivation, we assume that counterions are localized in the plane of the membrane. Thus our approach presented here is relevant to the strongly charged case. More precisely, the separation between plates is much larger than the Gouy-Chapman length, a typical length scale within which counterions are confined. The main purpose of the present work is to study the crossover from the high-temperature results for the membrane attractions to the behavior expected at low temperatures. Since this
crossover occurs at low temperatures or at high densities of counterions, the assumption of localized counterions is reasonable.

The charge distribution on a layer \( j \) is described by the local surface charge density \( \sigma_i(\mathbf{r}_\perp) = -e\sigma_0 + emZ \), where \( e \) is the electronic charge, \( \sigma_0 \) is the average counterion number density, \( m = 0, 1, 2, 3 \), etc., is the number of counterions per unit area at \( \mathbf{r}_\perp \equiv (x, y) \), and \( Z \) is the counterion valency. In order to calculate the free energy and the corresponding charge correlations (cf. Eq. \( \text{[2]} \)), we use two-dimensional Debye-Hückel (DH) theory. This approximation, however, fails to capture the strong charge-correlations at low temperatures. This defect in the DH approximation, however, fails to capture the strong charge-fluctuations contributions to the free energy per area is

\[
\frac{\Delta F_N}{k_B T} = \frac{1}{2} \int \frac{dk_{\perp}}{(2\pi)^2} \left\{ \log \left[ \det \left( Q(k_{\perp}) \right) \right] - N \frac{g(k_{\perp})}{\lambda k_{\perp}} \right\},
\]

where \( \lambda^{-1} = 2\pi Z\ell_B \sigma_0 \) is the inverse Gouy-Chapman length and \( \ell_B = e^2/ \varepsilon k_B T \) is the Bjerrum length, i.e. the length scale at which the electrostatic energy between two charges is comparable to the thermal energy. 

The matrix \( Q(k_{\perp}) \) is defined by the matrix elements

\[
Q_{ij}(k_{\perp}) = \delta_{ij} + \frac{g_{ij}(k_{\perp})}{\lambda k_{\perp}} e^{-k_{\perp} h_{ij}},
\]

where \( g_{ij}(k_{\perp}) \equiv g(k_{\perp}) \equiv \frac{2J_i(k_{\perp}D)}{k_{\perp}D} \) if \( i = j \) and 1 otherwise, and \( J_1(x) \) is the first-order Bessel function of the first kind. Finally, \( h_{ij} \) is the separation between plates \( i \) and \( j \).

First note that the free energy of an \( N \)-plate system is not simply a pairwise sum of the corresponding two-plate results over all pairs of plates. Thus the pairwise additivity is not always satisfied as will be detailed later. For the \( N = 2 \) case, our result in Eq. \( \text{[2]} \) reduces to the previous two-plate result [see Eq. 3 of Ref. \( \text{[3]} \)], if \( D \) is set to zero. When \( D = 0 \), the free energy has a single minimum at a nonzero value \( k_{\perp} = k_{\perp}^0 \ll 1\text{A}^{-1} \) for all values of \( \lambda \). The dominance of the long-wavelength charge fluctuations is responsible for the breakdown of the pairwise additivity of electrostatic interactions between macroions. It has been shown that the pairwise additivity for the case of charged rods breaks down if the expansion of the corresponding interaction free energy in powers of \( \ell_B \) diverges \([1, 2, 23]\). For rod systems, the free energy is dominated by the zero-\( k \) mode and thus this expansion converges only when the charge fluctuation along the rods is vanishingly small. For the two-dimensional case, the convergence of the \( \ell_B \)-expansion can be tested by estimating \( \delta \equiv (k_{\perp}^0)^{-1} \lambda^{-1} \); the \( \ell_B \)-expansion is convergent if \( \delta < 1 \). We, however, find that \( \delta \) is smaller for smaller values of \( \lambda^{-1} \) and is comparable to unity if \( \lambda^{-1} < 10^{-3} \). As in the rodlike systems, the pairwise additivity is violated unless the inverse of the Gouy-Chapman length is very small. Thus the pairwise additivity can easily be violated even in two-dimensional systems.

The above analysis, however, cannot be pursued when the temperature is low or when the density of ions is high. In this case, it is crucial to incorporate \( D \neq 0 \); the ion size constitutes an important length scale at low temperatures or at high density of ions. Having understood that the dominance of long-wavelength charge fluctuations for the case \( D = 0 \) leads to the breakdown of pairwise additivity, we now examine the low-\( T \) behavior of the free energy (thus with \( D \) set to a finite value) in Fourier space. Let us first consider the case of two plates separated by a distance \( h \). For convenience, we consider the following quantity:

\[
\mathcal{Q}(k_{\perp}) = k_{\perp} \log(\det(\mathbf{Q}(k_{\perp}))),
\]

as a function of \( k_{\perp} \) for several different values of the Gouy-Chapman length \( \lambda \). We have chosen \( D = 5\text{A} \) and \( h = 5\text{A} \). When \( \lambda^{-1} = 1\text{A}^{-1} \), the free energy has only one minimum at \( k_{\perp}^0 \ll 1\text{A}^{-1} \), while when \( \lambda^{-1} = 1.5\text{A}^{-1} \), the free energy has another local minima at \( k_{\perp} = k_{\perp}^0 = \mathcal{O}(1\text{A}^{-1}) \). When \( \lambda^{-1} = 7\text{A}^{-1} \), the second minima at large \( k_{\perp} \) is overwhelmingly dominant. When \( \lambda^{-1} = 10\text{A}^{-1} \), the free energy has two local minima at \( k_{\perp} \approx \mathcal{O}(1\text{A}^{-1}) \).

In Fig. 1, we plot this quantity \( \mathcal{Q}(k_{\perp}) \) as a function of \( k_{\perpendicular} \) for several different values of the Gouy-Chapman length \( \lambda \). We have chosen \( D = 5\text{A} \) and \( h = 5\text{A} \). When \( \lambda^{-1} = 1\text{A}^{-1} \), \( \mathcal{Q}(k_{\perpendicular}) \) has a single minimum at \( k_{\perpendicular} = k_{\perpendicular}^0 \ll 1\text{A}^{-1} \). This implies that the free energy is dominated by long-wavelength charge fluctuations as in the previous case of point charges. We find that the function \( \mathcal{Q}(k_{\perpendicular}) \) has two minima at \( k_{\perpendicular} = k_{\perpendicular}^0 \ll 1\text{A}^{-1} \) and at \( k_{\perpendicular} = k_{\perpendicular}^0 \approx \mathcal{O}(1\text{A}^{-1}) \), respectively, for \( \lambda^{-1} > 4.2\text{A}^{-1} \) (not shown in the figure). As \( \lambda^{-1} \) changes, the minimum at \( k_{\perpendicular} = k_{\perpendicular}^0 \) varies monotonically and is deeper for larger \( \lambda^{-1} \). The minimum at \( k_{\perpendicular} = k_{\perpendicular}^0 \), however, is roughly independent of \( \lambda \). When \( \lambda^{-1} \approx 5.9\text{A}^{-1} \), the two minima are comparable in magnitude.

![FIG. 1. The wavevector dependence of the interaction free energy between two plates separated by \( h = 5\text{A} \), as a function of \( k_{\perpendicular} \). We have chosen \( D = 5\text{A} \). When \( \lambda^{-1} = 1\text{A}^{-1} \), the free energy has only one minimum at \( k_{\perpendicular}^0 \ll 1\text{A}^{-1} \), while when \( \lambda^{-1} = 1.5\text{A}^{-1} \), the free energy has another local minima at \( k_{\perpendicular} = k_{\perpendicular}^0 \approx \mathcal{O}(1\text{A}^{-1}) \). When \( \lambda^{-1} = 7\text{A}^{-1} \), the second minima at large \( k_{\perpendicular} \) is overwhelmingly dominant. When \( \lambda^{-1} = 10\text{A}^{-1} \), the free energy has two local minima at \( k_{\perpendicular} \approx \mathcal{O}(1\text{A}^{-1}) \).](image)
the function $Q(k_\perp)$ is overwhelmingly dominated by the second minimum at $k_\perp = k_\perp^2$, as shown in the figure. At $\lambda^{-1} = \lambda_X^{-1} = 7.2 \text{Å}^{-1}$, the second minimum diverges. This is suggestive of the onset of crystallization of counterions as will be detailed later. Even though the region $\lambda^{-1} \geq \lambda_X^{-1}$ is certainly beyond the validity of our theory, it is nevertheless interesting to see what our theory implies for that region. Notably, the free energy curve corresponding to $\lambda^{-1} = 10 \text{Å}^{-1}$ has two local minima at large $k_\perp = O(1 \text{Å}^{-1})$. The existence of multiple minima at large $k_\perp$ assures that the system is in a solidlike phase.

Our results in Fig. 1 imply that there are two distinct contributions to the free energy: long-wavelength fluctuations and short-wavelength fluctuations in the density of counterions. They also imply that the short-wavelength fluctuation contribution to the free energy has a much narrower peak if $\lambda^{-1} \gg 5.9 \text{Å}^{-1}$. This enables us to separate the short-wavelength contribution from the long-wavelength contribution. By noting that $e^{-k_\perp^2 h}$ does not change appreciably over the region inside the peak at $k_\perp = k_\perp^2$, we find, up to $h$-independent terms

$$\Delta F_2 \approx -\frac{k_B T}{16\pi^2} \frac{\zeta(3)}{\hbar^2} \frac{k_\perp^{-1} d k_\perp}{1 + k_\perp^{-1} \lambda^{-1} g(k_\perp)^2},$$

(3)

where $\zeta(x)$ is the zeta function (thus $\zeta(3)/16\pi^2 \approx 0.024$). The first term denoted by $F_{LW}$ is the free energy calculated with $D = 5 \text{Å}$ and is the long-wavelength free energy. Our previous analysis on $Q(k_\perp)$ implies that the short-wavelength free energy denoted by $F_{SW}$, i.e., the second term in Eq. (3), is dominant over the long-wavelength free energy $F_{LW}$ at low temperatures ($\lambda^{-1} \gg 5.9 \text{Å}^{-1}$) and decays exponentially in space. The exponentially decaying interaction between two plates is consistent with the zero-$T$ analysis in Refs. [1,2,27]. At high temperatures corresponding to $\lambda^{-1} \ll 5.9 \text{Å}^{-1}$, however, the free energy is mainly determined by $F_{LW}$. In this case, the fluctuation contribution to the pressure between the two plates scales as $-h^{-3}$ [2,27]. Also note that this long-wavelength contribution vanishes at $T = 0$. This follows from the fact that $Q(k_\perp^2)$ is roughly independent of $\lambda$. To estimate the temperature dependence of $F_{SW}$, note that the prefactor of this term varies as $T^{-1}$. The $k_\perp$-integral of this term depends on the depth and width of the second minimum of $Q(k_\perp)$ at $k_\perp = k_\perp^2$. While the width is roughly independent of $\lambda$ for given $h$, the minimum becomes deeper with the increasing $\lambda$ (or decreasing $T$). This proves that $F_{SW}$ is more negative at low $T$ than at high $T$, as opposed to $F_{LW}$.

For a given value of $h$, there exists a special value $\lambda_{cr}$ at which the crossover between the two distinct behaviors of the plate interaction ($F_{LW}$ and $F_{SW}$) takes place. By requiring $\left. \frac{\partial}{\partial h} (F_{LW} - F_{SW}) \right|_{h = \lambda_{cr}} = 0$, we have the following transcendental equation for $\lambda_{cr}$:

$$\left( \frac{\pi}{2} \right) \frac{\zeta(3)}{k_\perp^2} \frac{e^{2k_\perp^2 h}}{\hbar^2} = \frac{1}{\lambda_{cr}^2} \int_{k_\perp \neq 0} \frac{k_\perp^{-1} d k_\perp}{1 + k_\perp^{-1} \lambda_{cr} g(k_\perp)^2}. \quad (4)$$

(4)

To solve the transcendental equation, we have chosen $D = 5 \text{Å}$. Fig. 2 describes distinct regimes characterized by the corresponding dominant modes of fluctuations, and the crossover boundaries between them; the regimes where the long-wavelength (LW) and short-wavelength (SW) fluctuations dominate are denoted by LW and SW, respectively. When $\lambda^{-1}$ is smaller than $2.7 \text{Å}^{-1}$, the plate interaction is solely determined by the LW fluctuations for the whole range of $h$. At $\lambda^{-1} \approx 2.7 \text{Å}^{-1}$, marked by the vertical dotted line on the left, the SW fluctuations start to contribute to the plate interaction. When $2.7 \text{Å}^{-1} \leq \lambda^{-1} \leq 7.6 \text{Å}^{-1}$, however, the plate interaction is determined by the competition between the two; the crossover from the LW to SW regime takes places for larger value of $h$ at low temperatures (corresponding to larger $\lambda^{-1}$). At $\lambda^{-1} = \lambda_X^{-1} \approx 7.6 \text{Å}^{-1}$ [24], marked by the vertical dotted line on the right, the crossover occurs only when $h \rightarrow \infty$. Beyond $\lambda_X^{-1}$, the SW fluctuations solely determine the plate interaction.

FIG. 2. Phase diagram for two plates. The regimes where long-wavelength and short-wavelength fluctuations dominate are denoted by LW and SW, respectively.

The appearance of two distinctive competing interactions, i.e., $F_{LW}$ and $F_{SW}$, can also be understood in terms of in-plane charge correlations for a single plate: $G_1 (r_\perp, r_\perp') = \langle \sigma(r_\perp) \sigma(r_\perp') \rangle - \langle \sigma(r_\perp) \rangle \langle \sigma(r_\perp') \rangle$. The long-wavelength contribution to the charge correlation was shown to scale as $G_{LW}(r_\perp, r_\perp') \sim -k_BT/|r_\perp - r_\perp'|^3$ [27]. Note that this correlation vanishes as $T \to 0$. Our result in Eq. (3) implies that the short-wavelength charge correlation function is given by

$$G_{SW}(r_\perp, r_\perp') \approx g(r_\perp, r_\perp'),$$

(5)
where $J_0(x)$ is the zeroth-order Bessel function of the first kind. Unlike the long-wavelength correlation, the behavior of the short-wavelength correlation is determined by the nature of the poles of $[1 + \lambda k_\perp/g(k_\perp)]^{-1}$. We find that $G_{SW}$ shows an oscillatory decay, and that the amplitude of $G_{SW}$ varies as $T^{-1} \left[ 1 + (k_\perp^2 \lambda)^{-1} g(k_\perp) \right]^{-1}$ and is larger at low temperatures. For the two-plate case, this oscillatory charge correlation essentially gives rise to the SW interaction.

At high temperatures, we can consider each plate to consist of large domains, i.e., counterion-rich and counterion-poor domains. The size of the domains is on the order of $(k_\perp^2 \lambda)^{-1} \gg 1\text{Å}$, and thus these domains can form huge dipoles, resulting in a long-ranged attraction. The long-wavelength fluctuations couple over many plates, leading to breakdown of pairwise additivity [28] in the $N$-plate case. We also find that the power-law behavior of the in-plane charge correlation crosses over to an exponential decaying form as $N \to \infty$ [29]. This is clearly suggestive of the breakdown of pairwise additivity. As the temperature decreases, however, the plate interaction driven by long-wavelength fluctuations crosses over to a distinct behaviour controlled by non-monotonically decaying charge correlations. At low temperatures, each domain becomes overall charge neutral and thus the distinction between domains is meaningless. In this case, the local correlation between a counterion and a backbone charge in its neighborhood dominates the free energy. There is thus strong cancellation of repulsions (between like charges) with attractions (between opposite charges). This results in an exponentially decaying, short-ranged attraction between the plates.

In conclusion, we have presented a systematic approach to study the nature of counterion-mediated attractions between fluid membranes. We have shown that the nature of these attractions is determined by the dominant modes of fluctuations in the density of counterions. At high temperatures, fluctuations at large length scales determine the membrane interactions; the resulting interactions are long-ranged and not pairwise additive. Charge densities of biomembranes range from 0.03 to 0.24/\text{nm}^2, corresponding to LW regimes at room temperature. It is thus clear that many-body, non-pairwise additive interactions operate in biomembrane systems at room temperature. At low temperatures, however, the membrane interactions are dominated by SW charge fluctuations and are exponentially decaying with the membrane spacing. In this case, only the nearest pairs of plates couple strongly with each other. Surprisingly, this implies that the pairwise additivity is restored at very low temperatures (the non-pairwise additive interaction becomes smaller, and eventually vanishes, as $T \to 0$).

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