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Effective Hamiltonian for fluid membranes in the presence of long-ranged forces

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If the constituent particles of fluid phases interact via long-ranged van der Waals forces, the effective Hamiltonian for interfaces between such fluid phases contains—in lateral Fourier space—nonanalytic terms $\sim q^4 \ln q$. Similar nonanalytic terms characterize the effective Hamiltonian for two interacting interfaces which can emerge between the three possible coexisting fluid phases in binary liquid mixtures. This is in contrast with the structure of the phenomenological Helfrich Hamiltonian for membranes, which does not contain such nonanalytic terms. We show that under favorable conditions for the bulk densities characterizing a binary liquid mixture and for the long-ranged interparticle interactions, the corresponding effective Hamiltonian for a model fluid membrane does not exhibit such nonanalytic contributions. We discuss the properties of the resulting effective Hamiltonian, with a particular emphasis on the influence of the long range of the interactions on the coefficient of the bending rigidity.

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I. INTRODUCTION

In order to be able to describe nonplanar configurations of interfaces and membranes, the derivation and use of corresponding effective Hamiltonians has been studied intensively [1–3]. Depending on the environment and their internal composition, interfaces and membranes can display rather complex behaviors [4]. A particular class of such systems is formed by the ubiquitous fluid-fluid interfaces and fluid membranes. In the case of interfaces, the effective Hamiltonian takes on a capillary-wave-like structure [5] while membranes are usually described in terms of the so-called Helfrich Hamiltonian [6].

On the phenomenological level, the effective Hamiltonian contains two types of contributions: the first is related to the possible change of the interface or membrane area and is controlled by the coefficient σ_0 of the surface tension, while the second contribution is proportional to the square of the local mean curvature of the interface or membrane and is controlled by the coefficient κ of the bending rigidity. In the following we consider fluctuating interfaces or membranes which are planar on the average and do not change their topology; thus contributions due to the Gaussian curvature do not matter. In lateral Fourier space, the contribution from the q mode, $\tilde{f}(\mathbf{q})$, of a local height configuration to the effective Hamiltonian is proportional to $|\tilde{f}(\mathbf{q})|^2 (qa)^2 \sigma(q)$, where a is a microscopic length scale proportional to the particle diameter and $\sigma(q\to 0)=\sigma_0+\kappa(qa)^2$.

Here we focus on the ensuing structure of the effective Hamiltonian for systems in which the interparticle interactions are of the long-ranged van der Waals type. This issue becomes acute if one tries to justify and to derive the phenomenological capillary-wave Hamiltonian from a microscopic theory such as, e.g., density functional theory [5]. In such approaches it turns out that for interfaces between fluid phases in systems governed by long-ranged forces the effective surface tension $\sigma(q)$ exhibits the form $\sigma(q\to 0)=\sigma_0+\sigma_1(qa)^2\ln(qa)+\kappa(qa)^2$, and thus contains a leading nonanalytic term $\sigma_1(qa)^2\ln(qa)$ with $\sigma_1>0$ that is not captured by phenomenological approaches. This logarithmic singularity in Fourier space can be traced back to the divergence of the third and higher moments of the interparticle interaction potentials decaying as a function of the distance $\sim r^{-6}$. For fluid interfaces the presence of such a nonanalytic contribution has been established theoretically [7–10]. This algebraic decay of the long-ranged van der Waals interactions leaves a trace also in the bulk structure such that the Fourier transform of the direct correlation function contains a nonanalytic term $\sim q^3$ [11–13]. For the interfaces considered here, the aforementioned logarithmic singularity in the interfacial structures implies that for small $q\neq 0$ one has $\sigma(q)<\sigma_0$. This decrease of $\sigma(q)$ for small q, which is consistent with the term $\sigma_1(qa)^2\ln(qa)$ in $\sigma(q)$, has been confirmed by several independent x-ray scattering experiments carried out for various fluids [14], as well as by some simulations [15] but not all [16]. On the other hand, such nonanalytic terms are absent in the effective Helfrich Hamiltonian for membranes which, however, successfully describes various properties of fluid membranes. This is puzzling because the particles making up membranes invariably also exhibit long-ranged van der Waals interactions, which in turn should lead to nonanalytical bending contributions.

Our objective is to construct a simple model of a fluid membrane based on the extension of a model of two interacting fluid-fluid interfaces. We want to check under which conditions, if any, the absence of nonanalytic terms of the type $\sigma_1(qa)^2\ln(qa)$ in the effective Hamiltonian for a membrane is possible, and what kind of influence on the remaining terms these conditions have. In the following section we recall the relevant results concerning the structure of the capillary-wave Hamiltonian. In Sec. III we discuss a simple model of fluid membranes in a system with long-ranged forces which is based on a model of two interacting fluid-

fluid interfaces in a binary liquid mixture. We establish the conditions under which the effective Hamiltonian for the fluid membrane is free from nonanalyticities present in the corresponding capillary-wave Hamiltonian for the interface and is thus compatible with the structure of the Helfrich Hamiltonian. In Sec. IV we compare our predictions for the resulting effective Hamiltonian with those discussed in the literature.

II. EFFECTIVE HAMILTONIAN FOR A FLUID-FLUID INTERFACE

In this section we recall the basic facts pertinent to the structure of the capillary-wave Hamiltonian $\mathcal{H}_{\mathrm{cw}}[f]$ for a fluid-fluid interface. Its local height relative to the reference plane $z=0$ is described by the function $z=f(\mathbf{R})$, where $\mathbf{R}=(x,y)$ denotes the lateral coordinates. Various aspects of this structure have been discussed in the literature. In particular, the issue of a local versus a nonlocal structure of $\mathcal{H}_{\mathrm{cw}}[f]$ has been extensively analyzed for the cases of short-ranged (exponentially) and long-ranged (algebraically) decaying interactions [7–10,17]. A suitable framework for analyzing such issues is density functional theory for nonuniform fluids. This analysis is particularly straightforward if the nonuniform one-component fluid density $\rho(\mathbf{R},z)$ associated with an interface configuration $f(\mathbf{R})$ is approximated within the so-called sharp-kink approximation by a piecewise constant function $\rho_{\mathrm{shk}}(\mathbf{R},z)=\rho_\beta\Theta(f(\mathbf{R})-z)+\rho_\alpha\Theta(z-f(\mathbf{R}))$, where ρ_α and ρ_β denote the bulk densities of the coexisting fluid phases α and β, and $\Theta(z)$ denotes the Heaviside function. If, moreover, the effective Hamiltonian is truncated to be bilinear in f, it can be written as [7–9] (in the Appendix we summarize the corresponding basic steps of the analysis)

$$\mathcal{H}_{\mathrm{cw}}[f]=\frac{1}{2}\int\frac{d^2q}{(2\pi)^2}|\tilde{f}(\mathbf{q})|^2q^2\sigma(q), \tag{1}$$

where

$$\tilde{f}(\mathbf{q})=\int d^2R\, f(\mathbf{R})\exp(-i\mathbf{q}\cdot\mathbf{R}). \tag{2}$$

The wave-vector-dependent surface tension $\sigma(q)$ in Eq. (1) is given by

$$\sigma(q)=q^{-2}[\tilde{w}(q)-\tilde{w}(0)](\rho_\alpha-\rho_\beta)^2, \tag{3}$$

where $\tilde{w}(q)$ denotes the Fourier transform of the long-ranged part of the spherically symmetric interparticle interaction potential $w(r=|(\mathbf{R},z)|)$ taken with respect to the lateral coordinates for $z=0$:

$$\tilde{w}(q)=\int d^2R\, w(|(\mathbf{R},z=0)|)\exp(-i\mathbf{q}\cdot\mathbf{R}). \tag{4}$$

It has turned out to be suitable to adopt for the long-ranged part of the van der Waals pair potential $w(\mathbf{R},z)$ the form

$$w(|(\mathbf{R},z)|)=-\frac{A}{(\mathbf{R}^2+z^2+a^2)^3}, \tag{5}$$

where a corresponds to the hard core radius of the fluid particles and $A>0$ characterizes the strength of the attractive interparticle interaction. For $\bar{q}=qa\ll 1$ the ensuing $\sigma(q)$ has the following nonanalytic form:

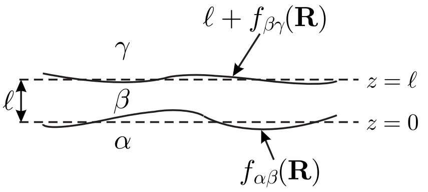

FIG. 1. The system under consideration consists of two fluid-fluid interfaces $f_{\alpha\beta}(\mathbf{R})$ and $\ell+f_{\beta\gamma}(\mathbf{R})$ separating the phases α, β and β, γ, respectively, and fluctuating around their mean positions $z=0$ and $z=\ell$, respectively.

$$\sigma(q)=\sigma_0+\sigma_1\bar{q}^2\ln(\bar{q})+\sigma_2\bar{q}^2+O(\bar{q}^4), \tag{6}$$

where $\sigma_0=(A\pi/8a^2)(\rho_\alpha-\rho_\beta)^2>0$, $\sigma_1=\frac{1}{4}\sigma_0>0$, $\sigma_2=\frac{1}{4}\sigma_0C_0<0$, $C_0=C_{\mathcal{E}}-3/4-\ln 2=-0.866$, and $C_{\mathcal{E}}$ denotes Euler's constant.

A more realistic approach to determine $\sigma(q)$ [9] takes into account the influence of local interfacial curvatures on the actual smooth intrinsic density profile. The effective Hamiltonians for interfaces both in one-component [9] and in binary liquid mixtures [10] have been analyzed along these lines. For long-ranged van der Waals interactions in each case the presence of nonanalytic terms in $\sigma(q)$ [Eq. (1)] has been established.

III. A MODEL OF A FLUID MEMBRANE

For the comparison between effective Hamiltonians for fluid-fluid interfaces and fluid membranes it is particularly suitable to consider binary liquid mixtures. Upon special choices of the thermodynamic conditions these systems allow for the coexistence of three fluid phases denoted as α, β, and γ. In the presence of appropriately chosen boundary conditions or external ordering fields one can consider a situation in which a layer of—say—phase β with mean thickness ℓ separates the phases α and γ [18]. In such a system there are two fluid-fluid interfaces, the positions of which are denoted by $f_{\alpha\beta}(\mathbf{R})$ and $\ell+f_{\beta\gamma}(\mathbf{R})$. They separate the phases α, β and β,γ, respectively (see Fig. 1). We note that, although the system is characterized by six number densities $\rho_{i\lambda}$, with $i=1,2$, and $\lambda=\alpha,\beta,\gamma$, where $\rho_{i\lambda}$ denotes the number density of the ith component in phase λ, three-phase coexistence allows for only one independent thermodynamic variable such as temperature; on the corresponding triple line the chemical potentials $\mu_1(T)$ and $\mu_2(T)$ of the two species are fixed. In addition, there are three interparticle interactions present in the system: two among the two species and one between the different species. They are assumed to be spherically symmetric and are denoted by $w_{ij}(r)=w_{ji}(r)=w_{ij}(|(\mathbf{R},z)|)$ with $i,j=1,2$.

For such a system containing two interfaces, the capillary-wave Hamiltonian $\mathcal{H}_{\mathrm{cw}}([f_{\alpha\beta},f_{\beta\gamma}],\ell)$ is a functional of the two interfacial positions $f_{\alpha\beta}(\mathbf{R})$ and $f_{\beta\gamma}(\mathbf{R})$ and a function of the distance ℓ. Application of the sharp-kink approximation to the density functional for binary liquid mixtures described, e.g., in Refs. [8,10] yields within the bilinear approximation, which retains nonlocality, the following form (see the Appendix):

$$\mathcal{H}_{\mathrm{cw}}([f_{\alpha\beta},f_{\beta\gamma}],\ell)=\frac{1}{2}\int\frac{d^2q}{(2\pi)^2}\{2\tilde{f}_{\alpha\beta}(\mathbf{q})\tilde{f}_{\beta\gamma}(-\mathbf{q})\tilde{w}_{\alpha\beta,\beta\gamma}(q,\ell)+|\tilde{f}_{\alpha\beta}(\mathbf{q})|^2[q^2\sigma_{\alpha\beta}(q)-\tilde{w}_{\alpha\beta,\beta\gamma}(0,\ell)]+|\tilde{f}_{\beta\gamma}(\mathbf{q})|^2[q^2\sigma_{\beta\gamma}(q)-\tilde{w}_{\alpha\beta,\beta\gamma}(0,\ell)]\}, \tag{7}$$

where

$$\tilde{w}_{\lambda\kappa,\eta\delta}(q,z)=\sum_{i,j=1}^{2}(\rho_{i\lambda}-\rho_{i\kappa})(\rho_{j\eta}-\rho_{j\delta})\times\int d^2R\,\exp(-i\mathbf{q}\cdot\mathbf{R})w_{ij}(\mathbf{R},z) \tag{8}$$

and [8,10]

$$\sigma_{\lambda\kappa}(q)=q^{-2}[\tilde{w}_{\lambda\kappa,\lambda\kappa}(q,z=0)-\tilde{w}_{\lambda\kappa,\lambda\kappa}(q=0,z=0)]. \tag{9}$$

The above results can serve as a starting point to construct a simple model of a fluid membrane. To this end we take the two interface configurations to be in phase, i.e., $f_{\alpha\beta}(\mathbf{R})=f_{\beta\gamma}(\mathbf{R})$. This renders a model fluid membrane consisting of phase β embedded on one side by phase α and on the other side by phase γ. The thickness ℓ of the membrane is uniform and its upper and lower boundaries have the same shape described by $f(\mathbf{R})=f_{\alpha\beta}(\mathbf{R})=f_{\beta\gamma}(\mathbf{R})$. In this case and within the bilinear approximation the capillary-wave Hamiltonian reduces to

$$\mathcal{H}([f],\ell)=\frac{1}{2}\int\frac{d^2q}{(2\pi)^2}|\tilde{f}(\mathbf{q})|^2\gamma(q)q^2 \tag{10}$$

with

$$q^2\gamma(q)=\sum_{i,j=1}^{2}\{[(\rho_{i\alpha}-\rho_{i\beta})(\rho_{j\alpha}-\rho_{j\beta})+(\rho_{i\beta}-\rho_{i\gamma})(\rho_{j\beta}-\rho_{j\gamma})]\times[\tilde{w}_{ij}(q,0)-\tilde{w}_{ij}(0,0)]+2(\rho_{i\alpha}-\rho_{i\beta})(\rho_{j\beta}-\rho_{j\gamma})\times[\tilde{w}_{ij}(q,\ell)-\tilde{w}_{ij}(0,\ell)]\}. \tag{11}$$

With the choice

$$w_{ij}(|(\mathbf{R},z)|)=-\frac{A_{ij}}{(\mathbf{R}^2+z^2+a_{ij}^2)^3} \tag{12}$$

for the long-ranged interparticle potentials, one has

$$\tilde{w}_{ij}(q,\ell)-\tilde{w}_{ij}(0,\ell)=\frac{\pi}{8}A_{ij}\left(\frac{q^2}{a_{ij}^2+\ell^2}+\frac{q^4}{4}[\ln(q\sqrt{a_{ij}^2+\ell^2})+C_0]\right). \tag{13}$$

For reasons of simplicity in the following we assume $a_{ij}=a$, $i,j=1,2$. This choice leads to the following expression for $\gamma(q)$:

$$\gamma(q)=\gamma_0+\gamma_1\bar{q}^2\ln\bar{q}+\gamma_2\bar{q}^2+O(\bar{q}^4), \tag{14}$$

where, with $\bar{\ell}=\ell/a$,

$$\gamma_0(\ell)=\frac{\pi}{8a^2}\sum_{i,j=1}^{2}A_{ij}\left([(\rho_{i\alpha}-\rho_{i\beta})(\rho_{j\alpha}-\rho_{j\beta})+(\rho_{i\beta}-\rho_{i\gamma})\times(\rho_{j\beta}-\rho_{j\gamma})]+\frac{2}{1+\bar{\ell}^2}(\rho_{i\alpha}-\rho_{i\beta})(\rho_{j\beta}-\rho_{j\gamma})\right), \tag{15}$$

$$\gamma_1=\frac{\pi}{32a^2}\sum_{i,j=1}^{2}A_{ij}(\rho_{i\alpha}-\rho_{i\gamma})(\rho_{j\alpha}-\rho_{j\gamma}), \tag{16}$$

and

$$\gamma_2(\ell)=\frac{\pi}{32a^2}\sum_{i,j=1}^{2}A_{ij}[\ln(1+\bar{\ell}^2)(\rho_{i\alpha}-\rho_{i\beta})(\rho_{j\beta}-\rho_{j\gamma})+C_0(\rho_{i\alpha}-\rho_{i\gamma})(\rho_{j\alpha}-\rho_{j\gamma})]. \tag{17}$$

As expected, similar to the case of a single interface [Eq. (6)], the effective Hamiltonian for the model fluid membrane contains a nonanalytic contribution $\gamma_1\bar{q}^4\ln\bar{q}$. In this sense the structure of the effective Hamiltonian given by Eqs. (10) and (14)–(17) is not compatible with the phenomenological Helfrich Hamiltonian ansatz which for small membrane undulations can be expressed in a form as in Eq. (14) but with $\gamma_1=0$.

Our purpose is thus to find conditions under which the coefficient γ_1 of the nonanalytic contribution in Eq. (14) vanishes. There are two particularly simple choices of the number densities $\rho_{i\lambda}$ and the amplitudes A_{ij} of the interaction potentials which satisfy this requirement. The first choice (I) puts constraints on the densities of the phases α and γ and stipulates

$$\rho_{i\alpha}=\rho_{i\gamma},\quad i=1,2\quad (\mathrm{I}). \tag{18}$$

This condition requires that the two phases on both sides of the membrane are identical. The second choice (II) puts constraints both on the interaction amplitudes and on the densities. First, it requires that

$$A_{12}=\sqrt{A_{11}A_{22}}\quad (\mathrm{IIa}), \tag{19}$$

which leads to

$$\gamma_1=\frac{\pi}{32a^2}[\sqrt{A_{11}}(\rho_{1\alpha}-\rho_{1\gamma})+\sqrt{A_{22}}(\rho_{2\alpha}-\rho_{2\gamma})]^2. \tag{20}$$

The additional requirement

$$\sqrt{A_{11}}(\rho_{1\alpha}-\rho_{1\gamma})=-\sqrt{A_{22}}(\rho_{2\alpha}-\rho_{2\gamma})\quad (\mathrm{IIb}) \tag{21}$$

implies $\gamma_1=0$. It is straightforward to show that the above condition I [Eq. (18)] leads to

$$\gamma^{(\mathrm{I})}(q)=\frac{\pi}{4a^2}[\sqrt{A_{11}}(\rho_{1\alpha}-\rho_{1\beta})+\sqrt{A_{22}}(\rho_{2\alpha}-\rho_{2\beta})]^2\varphi(\bar{q},\bar{\ell}), \tag{22}$$

where

$$\varphi(\bar{q},\bar{\ell}) = \frac{\bar{\ell}^2}{1+\bar{\ell}^2} - \frac{\bar{q}^2}{8}\ln(1+\bar{\ell}^2). \tag{23}$$

Interestingly, if the conditions IIa [Eq. (19)] and IIb [Eq. (21)] are imposed, the corresponding effective surface tension $\gamma^{(\mathrm{II})}(q)$ has exactly the same form as for the first condition, i.e., $\gamma^{(\mathrm{II})}(q)=\gamma^{(\mathrm{I})}(q)$. The fact that the requirements II, which put constraints on both the densities and the interaction amplitudes, lead to the same result as the requirement I, which identifies the phases α and γ but does not involve the interaction amplitudes A_{ij}, can be understood as follows. We consider a typical contribution to the free energy density functional which describes the interaction between particles located in a region $\mathcal{V}_\alpha$ of the binary liquid mixture with a specific particle of type k, $k=1,2$, located at $\mathbf{r}'$ somewhere in the system. This term is proportional to

$$\begin{aligned}\int_{\mathcal{V}_\alpha} d^3r\sum_i w_{ik}(\mathbf{r}-\mathbf{r}')\rho_{i\alpha} &\sim \sum_i A_{ik}\rho_{i\alpha}\\ &= A_{1k}\rho_{1\alpha}+A_{2k}\rho_{2\alpha}\\ &= \sqrt{A_{kk}}(\sqrt{A_{11}}\rho_{1\alpha}+\sqrt{A_{22}}\rho_{2\alpha})\\ &= \sqrt{A_{kk}}(\sqrt{A_{11}}\rho_{1\gamma}+\sqrt{A_{22}}\rho_{2\gamma})\\ &= A_{1k}\rho_{1\gamma}+A_{2k}\rho_{2\gamma},\end{aligned} \tag{24}$$

where the conditions in Eqs. (19) and (21) have been used. One concludes that this contribution to the free energy functional has the same form as if the region $\mathcal{V}_\alpha$ were filled with particles with densities $\rho_{i\gamma}$ instead of $\rho_{i\alpha}$. But this is exactly the requirement in Eq. (18) corresponding to choice I which identifies the phases α and γ.

In the next section we discuss the properties of the resulting effective Hamiltonian.

IV. DISCUSSION

In the previous section we showed that for special choices for the densities or the interparticle interactions in binary liquid mixtures there are no nonanalytic contributions to $\gamma(q)$ in the limit of small q [up to and including $O(q^2)$]. This choice eliminates the leading nonanalytic contribution for any membrane thickness ℓ, because γ_1 does not depend on ℓ [see Eq. (16)]. It turns out that, independent of whether constraints of type I in Eq. (18) or of type II in Eqs. (19) and (21) are imposed, the resulting effective Hamiltonian for the model fluid membrane takes the form given by Eqs. (10) and (22). The function $\gamma^{(\mathrm{I})}(q)$ in Eq. (22) is determined by the bulk number densities $\rho_{i\lambda}$, $i=1,2$, $\lambda=\alpha,\beta$, the interaction strengths A_{11}, A_{22}, the particle size a, and the membrane thickness ℓ. The function $\gamma^{(\mathrm{I})}(q)$ factorizes into a product of two functions. The first factor depends on the densities and interaction strengths only and is non-negative. The second factor depends on $\bar{q}$ and parametrically on $\bar{\ell}$ only; the parameter a sets the scale for the variables q and ℓ. This second factor, which we denoted as $\varphi(\bar{q},\bar{\ell})$, is particularly interesting because—in contrast to the first factor—it can change sign depending on the values of $\bar{q}$ and $\bar{\ell}$. This possibility of $\gamma^{(\mathrm{I})}(q)$ changing sign appears because the coefficient γ_2 in Eq. (14) is inherently negative, i.e., the contribution from the long-ranged forces to the coefficient of the bending rigidity is negative. Note that within the sharp-kink approximation, which takes only the influence of the long-ranged forces into account, σ_2 is also negative [see Eq. (6) and the expressions following it]. This conclusion checks qualitatively with a recent analysis by Dean and Horgan [19], who have expressed the coefficient of the bending rigidity in terms of the membrane thickness and the dielectric constants of the membrane (ϵ) and of the surrounding medium (ϵ'):

$$\gamma_2^{\mathrm{DH}}(\ell) = -\frac{3k_BT}{128\pi}\left(\frac{\epsilon-\epsilon'}{\epsilon+\epsilon'}\right)^2\ln(1+\bar{\ell}^2). \tag{25}$$

Dean and Horgan [19] did not discuss the issue of the presence of nonanalytic terms in the effective Hamiltonian. However, our result and those in [19] agree concerning the functional form of the dependence of the coefficient $\gamma_2(\ell)$ on the membrane thickness ℓ. Within both approaches the coefficient of the bending rigidity depends logarithmically on the membrane thickness, i.e., $\gamma_2 \sim \ln(1+\bar{\ell}^2)$. Of course realistic membrane models yield additional contributions to the bending rigidity stemming from other types of interactions present in the system. In our approach only the long-ranged contributions to the bending rigidity are considered. In this latter case, the negative coefficient γ_2 of the bending rigidity in the presence of the positive coefficient γ_0 of the surface tension leads to an instability at small wavelengths of the membrane undulations. According to Eq. (23) this instability occurs for

$$\bar{q}^2 > \frac{8\bar{\ell}^2}{(1+\bar{\ell}^2)\ln(1+\bar{\ell}^2)} \quad (\text{unstable; I, II}). \tag{26}$$

On the other hand the wave vectors must be smaller than the physically allowed maximal one $\bar{q}_{\max} \lesssim 1$. This implies that the values of $\bar{\ell}$ for which the instability can occur satisfy the condition

$$\bar{\ell} > \bar{\ell}_0 = \exp\left(\frac{4}{\bar{q}_{\max}^2}\right) \quad (\text{unstable; I, II}). \tag{27}$$

For $\bar{q}_{\max}=1/2$ one has $\bar{\ell}_0=9\times10^6$. If, as an example, one takes the parameter a equal to the noble gas atomic size, say $a=0.1$ nm, then the above estimate gives $\ell_0=\bar{\ell}_0 a=0.9$ mm. This condition states that for membrane thicknesses $0<\bar{\ell}<\bar{\ell}_0$ the negative bending rigidity coefficient does not give rise to instabilities for membrane undulations with wave vectors within the physically accessible range $\bar{q}<\bar{q}_{\max}$.

Finally, we mention that the vanishing of the coefficient γ_1 can also occur in binary liquid mixtures in which the interactions w_{11} and w_{22} are repulsive, i.e., $A_{11}, A_{22}<0$, while the interactions w_{12} are attractive, i.e., $A_{12}>0$. (It is conceivable that such a situation may arise in multicomponent complex fluids with effective interactions between two dominating species upon integrating out the degrees of freedom of the smaller species. This can occur if the two species are oppositely charged.) This is a different situation from the one considered above in which all long-ranged interactions were assumed to be attractive, i.e., $A_{11}, A_{22}, A_{12} > 0$. In this present case the conditions IIa and IIb are replaced by

$$A_{12} = \sqrt{(-A_{11})(-A_{22})} \quad \text{(IIIa)} \tag{28}$$

so that

$$\gamma_1 = -\frac{\pi}{32a^2}[\sqrt{-A_{11}}(\rho_{1\alpha}-\rho_{1\gamma}) - \sqrt{-A_{22}}(\rho_{2\alpha}-\rho_{2\gamma})]^2, \tag{29}$$

and by

$$\sqrt{-A_{11}}(\rho_{1\alpha}-\rho_{1\gamma}) = \sqrt{-A_{22}}(\rho_{2\alpha}-\rho_{2\gamma}) \quad \text{(IIIb)}, \tag{30}$$

respectively. It is straightforward to see that in this case the effective surface tension denoted as $\gamma^{(\mathrm{III})}(q)$ is given by

$$\gamma^{(\mathrm{III})}(q) = -\frac{\pi}{4a^2}[\sqrt{-A_{11}}(\rho_{1\alpha}-\rho_{1\beta}) - \sqrt{-A_{22}}(\rho_{2\alpha} - \rho_{2\beta})]^2 \varphi(\bar{q},\bar{\ell}). \tag{31}$$

Accordingly, the model fluid membrane is unstable with respect to long-wavelength undulations:

$$\bar{q}^2 < \frac{8\bar{\ell}^2}{(1+\bar{\ell}^2)\ln(1+\bar{\ell}^2)} \quad \text{(unstable; III)}. \tag{32}$$

This implies that for undulations with given $\bar{q}$ values only membranes with thicknesses

$$\bar{\ell} < \exp\left(\frac{4}{\bar{q}^2}\right) \quad \text{(unstable; III)} \tag{33}$$

are unstable.

To summarize, we have shown that it is possible to choose conditions under which the leading nonanalytic contribution to the effective Hamiltonian of a fluid membrane in the presence of long-ranged forces vanishes. One of them amounts to the requirement that the embedding phases on both sides of a fluid membrane are identical. For example, if our conclusions are applied to the case of lipid membranes surrounded by water on both sides, the nonanalytic terms in the effective Hamiltonian should be absent. We have also checked that the contribution from long-ranged forces to the coefficient of the bending rigidity is negative, and we have discussed the implications for the stability of membranes with respect to undulations.

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APPENDIX: THE EFFECTIVE CAPILLARY-WAVE HAMILTONIAN FOR MULTICOMPONENT SYSTEMS

One way to derive the capillary-wave Hamiltonian for a two-component fluid mixture is to start from the mean-field-like grand canonical density functional [5,8]:

$$\Omega = \int d^3r\, f_{\mathrm{hs}}(\rho_1(\mathbf{r}),\rho_2(\mathbf{r}),T) + \frac{1}{2}\sum_{i,j=1}^{2}\int d^3r \int d^3r'\, w_{ij}(|\mathbf{r}-\mathbf{r}'|)\rho_i(\mathbf{r})\rho_j(\mathbf{r}') - \sum_{i=1}^{2}\mu_i \int d^3r\, \rho_i(\mathbf{r}), \tag{A1}$$

where $f_{\mathrm{hs}}(\rho_1(\mathbf{r}),\rho_2(\mathbf{r}),T)$ is the free energy density of the hard sphere reference fluid evaluated within the local density approximation; μ_i and $\rho_i(\mathbf{r})$ denote the chemical potential and the number density of the ith species, respectively. The interparticle interaction $w_{ij}(\mathbf{r}) = w_{ji}(r)$ is taken to be spherically symmetric. One encloses the mixture in a finite ($L_x \times L_y \times L_z$) box (Fig. 1) and evaluates the functional Ω [Eq. (A1)] for fixed positions of the interfaces $f_{\alpha\beta}$ and $\ell + f_{\beta\gamma}$ separating the coexisting phases α, β, and γ in the inhomogeneous system, using e.g., the sharp-kink approximation of steplike varying density profiles. After subtracting from Ω the appropriate bulk contributions, the contributions stemming from two reference planar interfaces, as well as both surface and line contributions induced by the interaction of the fluid with the enclosing walls, in the limit of infinite system size one is left with the capillary-wave Hamiltonian corresponding to two collective interfacial degrees of freedom:

$$\mathcal{H}_{\mathrm{cw}}([f_{\alpha\beta},f_{\beta\gamma}],\ell) = \mathcal{H}_0[f_{\alpha\beta}] + H_0[f_{\beta\gamma}] + \mathcal{H}_{\mathrm{I}}([f_{\alpha\beta},f_{\beta\gamma}],\ell). \tag{A2}$$

The first two terms on the right-hand side of Eq. (A2) are the Hamiltonians of the corresponding freely fluctuating interfaces:

$$\mathcal{H}_0[f_{\eta\delta}] = -\frac{1}{2}\int d^2R \int d^2R' \int_0^\infty dz \times \int_0^{f_{\eta\delta}(\mathbf{R}')-f_{\eta\delta}(\mathbf{R})} dz'\, w_{\eta\delta,\eta\delta}(|\mathbf{r}'-\mathbf{r}|), \tag{A3}$$

where

$$w_{\lambda\kappa,\eta\delta}(r) = \sum_{i,j=1}^{2}(\rho_{i\lambda}-\rho_{i\kappa})(\rho_{j\eta}-\rho_{j\delta})w_{ij}(r). \tag{A4}$$

That part of the Hamiltonian which describes the effective interaction between the two interfaces takes the form

$$H_{\mathrm{I}}([f_{\alpha\beta},f_{\beta\gamma}],\ell) = \int d^2R \int d^2R' \int_0^\infty dz \times \int_0^{f_{\beta\gamma}(\mathbf{R}')-f_{\alpha\beta}(\mathbf{R})} dz'\, w_{\alpha\beta,\beta\gamma}(|(\mathbf{R}'-\mathbf{R}, z' + z + \ell)|). \tag{A5}$$

After introducing the lateral Fourier transforms

$$\tilde{f}(\mathbf{q}) = \int d^2R \exp(-i\mathbf{q}\cdot\mathbf{R}) f(\mathbf{R}),$$

$$\tilde{w}_{ij}(q,z) = \int d^2R \exp(-i\mathbf{q}\cdot\mathbf{R}) w_{ij}(|(\mathbf{R},z)|), \qquad \text{(A6)}$$

the capillary-wave Hamiltonian in Eq. (A2) can be rewritten as

$$\begin{aligned}\mathcal{H}_{\mathrm{cw}}([f_{\alpha\beta},f_{\beta\gamma}],\ell) = \frac{1}{2}\int \frac{d^2q}{(2\pi)^2}\{&2\tilde{f}_{\alpha\beta}(\mathbf{q})\tilde{f}_{\beta\gamma}(-\mathbf{q})\tilde{w}_{\alpha\beta,\beta\gamma}(q,\ell)\\ &+|\tilde{f}_{\alpha\beta}(\mathbf{q})|^2[q^2\sigma_{\alpha\beta}(q)-\tilde{w}_{\alpha\beta,\beta\gamma}(0,\ell)]\\ &+|\tilde{f}_{\beta\gamma}(\mathbf{q})|^2[q^2\sigma_{\beta\gamma}(q)-\tilde{w}_{\alpha\beta,\beta\gamma}(0,\ell)]\},\end{aligned} \qquad \text{(A7)}$$

where

$$\begin{aligned}\tilde{w}_{\lambda\kappa,\eta\delta}(q,z) = \sum_{i,j=1}^{2}&(\rho_{i\lambda}-\rho_{i\kappa})(\rho_{j\eta}-\rho_{j\delta})\\ &\times\int d^2R \exp(-i\mathbf{q}\cdot\mathbf{R}) w_{ij}(|(\mathbf{R},z)|)\end{aligned} \qquad \text{(A8)}$$

and

$$\sigma_{\lambda\kappa}(q) = q^{-2}[\tilde{w}_{\lambda\kappa,\lambda\kappa}(q,z=0) - \tilde{w}_{\lambda\kappa,\lambda\kappa}(q=0,z=0)]. \qquad \text{(A9)}$$

The capillary-wave Hamiltonian for a single fluid-fluid interface [Eq. (1)] separating phases α and β can be obtained as a special case by setting $\gamma\equiv\beta$ and $\tilde{f}_{\alpha\beta}(\mathbf{q})\equiv\tilde{f}(\mathbf{q})$, or by setting $\ell\equiv 0$, $\tilde{f}_{\alpha\beta}(\mathbf{q})=\tilde{f}_{\beta\gamma}(\mathbf{q})\equiv\tilde{f}(\mathbf{q})$ in the above formulas.

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