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Interaction in colloidal systems: Buckling and melting

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The explicit form of the colloidal particle interaction has been calculated in restricted colloidal systems. Based upon the exact interaction, effects of buckling of the monolayer of colloidal particles in the middle of the electrolyte film is considered and the melting condition of colloidal crystals is found. Thermal fluctuations of inner degrees of freedom of the edge dislocation are shown to affect the condition of the dislocation-mediated melting.

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I. INTRODUCTION

One important question of the physics of colloidal systems refers to the determination of the effective interaction potential between colloidal particles [1]. In particular, the electrostatic interaction between highly charged particles in solution has been the subject of long-standing interest [2,3]. These interactions determine the static structural and dynamical properties of a colloidal liquid [4], crystallization of a colloidal liquid [5], and other phenomena.

Through dissociation, a colloidal particle acquires from the electrostatic surround the electric charge $q=Ne$, and in the three-dimensional bulk electrolyte the interparticle interaction can be well described by the screened Coulomb potential $(q^2/r)\exp(-r/\lambda_0)$ (Yukawa potential), where λ_0 is the Debye-Hückel radius. Under some circumstances, in experiment, the electrolyte bath is geometrically restricted, and charged colloidal particles interact partly through the outside region, which can be dielectric or vacuum. This can drastically change the Yukawa interaction potential. In this situation, the interaction potential for particles on the electrolyte surface has been written in an implicit way through the integral of the Bessel function [6]. In this paper, which uses methods of analytical functions, the explicit formulas for the interaction of colloidal particles have been found. The only restriction is the consideration of particles as pointlike objects (particle size smaller than the interparticle distance) and the linearized Poisson-Boltzmann equation (temperature higher than the interaction potential). Although quantitatively the resulting expression for the pair potential may only be exact at interparticle separations much larger than the particles diameter, for most of the thermodynamics and structural properties of interest this is the most relevant part of the repulsive electrostatic interaction. In fact, as is well known in the bulk three-dimensional case, the simple Yukawa functional form above provides a very accurate representation of the pair interaction [4]. Furthermore, more detailed derivations [3], in which the restrictions above (i.e., pointlike ions and the linearized Poisson-Boltzmann equation, etc.) are relaxed, lead essentially to the same functional form of the pair potential, differing only in the detailed definition of the amplitude of the Yukawa potential, which in many applications is treated as a fitting parameter associated with the effective macroparticle charge.

Melting of colloidal crystals has been observed experimentally [5]. In Refs. [5(a) and 5(b)] a loose translational and orientational order for suspensions of colloidal particles has been observed. Earlier work (Ref. [5(c)]) reported the existence of the crystalline and the disordered structures in the colloidal system on the water-air interface. A detailed picture of dislocation-mediated transitions in an analogous system is presented in Ref. [5(d)]. In our paper we study precisely the dependence of the condition for colloidal system melting (loose for a quasi–long-range translational order) on particle density, particle charge, and the Debye screening length, taking into account nontopological fluctuations. To observe the contribution of these fluctuations, further detailed measurements are required. One possible way to do this is to observe experimentally the melting condition for different particle concentrations and the chemical composition of the colloidal liquid, which influence directly the Debye length.

In Sec. II the systematic calculation of the particle interaction is given. We consider particles on an interface between vacuum and an electrolyte, particles in a thin film of electrolyte, and particles in the middle of a thick film of electrolyte.

In Sec. III the buckling of the particle monolayer in the middle of a film is considered. This effect has been calculated and experimentally observed in the systems of vortices in a type 2 superconductor [7]. In a colloidal system buckling has been considered in Ref. [8] for the Yukawa model particle interaction.

In Sec. IV the melting of a colloidal crystal is considered based upon the derived particle interaction. The phase diagram of dislocation-mediated melting [9–13] can provide information on particle interaction. See also [14].

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In Sec. V the effect of inner degrees of freedom of a dislocation on the melting condition is considered. The conventional condition of dislocation-mediated melting treats a dislocation as a "black box," considering only its translational degrees of freedom. As shown in Sec. V, thermal fluctuations of inner degrees of freedom of this black box can essentially change the melting condition.

II. INTERPARTICLE BETWEEN COLLOIDAL PARTICLES

We will consider a system of colloidal particles in the electrolyte medium. Each particle can be treated as a charged sphere of charge $q=Ne$, where N can be of the order of 100. The radius of the colloidal particles is considered to be small compared to the interparticle distance. This enables us to consider a colloidal particle as a point charge, omitting effects of the charge distribution over the particle surface.

Let us calculate the electrostatic potential $\varphi_u(\vec{r},z)$, produced at a point $(\vec{r},z)$, with $\vec{r}=x\hat{i}+y\hat{j}$, by the charged particle placed in the electrolyte at the point $\vec{r}=0$, $z=u$ (Fig. 1). The electrolyte fills the space between two parallel plates located at $z=\pm d$. Outside the electrolyte, a vacuum, or some other dielectric medium, is supposed to fill the remaining space $|z|>d$.

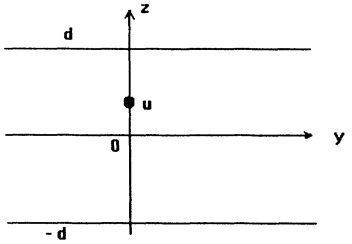

FIG. 1. The electrolyte fills in the space $|z|<d$. $|z|=u$ is the position of a particle.

The electrostatic potential satisfies the linearized Poisson-Boltzmann equation [15]

$$-\nabla^2\varphi_u+\frac{\varphi_u}{\lambda_0^2}\Theta(d^2-z^2)=4\pi q\delta(\vec{r})\delta(z-u)\ . \tag{2.1}$$

The solution can easily be found by using the Fourier transformation and matching solutions at boundaries. The result for $|z|<d$ is

$$\varphi_u(\vec{r},z)=2\pi q\int\frac{d^2k}{(2\pi)^2}\frac{e^{i\vec{k}\cdot\vec{r}}}{k_0}\left[\exp(-|z-u|k_0)+\left[1-\frac{k}{k_0}\right]\exp(-dk_0)\right.$$
$$\left.\times\left[\frac{\cosh(uk_0)\cosh(zk_0)}{\sinh(dk_0)+(k/k_0)\cosh(dk_0)}+\frac{\sinh(uk_0)\sinh(zk_0)}{\cosh(dk_0)+(k/k_0)\sinh(dk_0)}\right]\right]\ , \tag{2.2}$$

where $k_0=\sqrt{k^2+\lambda_0^{-2}}$. Let us consider some particular cases according to geometrical constrictions of specific experiments.

(i) Colloidal particles on the vacuum-electrolyte interface. In this case one can put $z=u=d$ and $d=\infty$ in Eq. (2.2) in order to obtain the interaction potential of two particles on the surface between the half-space of the vacuum and the half-space of the electrolyte. The interaction potential $V(\vec{r})=\lim_{d\to\infty}q\varphi_d(\vec{r},z)$ is

$$V(\vec{r})=4\pi q^2\int\frac{d^2k}{(2\pi)^2}\frac{e^{i\vec{k}\cdot\vec{r}}}{k+\sqrt{k^2+\lambda_0^{-2}}}\ . \tag{2.3}$$

Let us make the angular integration. This gives

$$V(r)=2q^2\int_0^\infty\frac{k\,dk}{k+\sqrt{k^2+\lambda_0^{-2}}}J_0(kr)=\frac{q^2\lambda_0^2}{\pi}\int_{-\infty}^{\infty}dk_y e^{ik_y y}\int_{-\infty}^{\infty}dk_x e^{ik_x x}\left(\sqrt{k_x^2+k_y^2+\lambda_0^{-2}}-\sqrt{k_x^2+k_y^2}\right)\ . \tag{2.4}$$

Deforming the k_x contour from the real axis to the complex plane, one can obtain

$$V(r)=\frac{2q^2\lambda_0^2}{\pi}\int_{-\infty}^{\infty}dk_y e^{ik_y y}\left[\int_{|k_y|}^{\infty}dk_x e^{-ik_x|x|}\sqrt{k_x^2-k_y^2}-\int_{k'}^{\infty}dk_x e^{-ik_x|x|}\sqrt{k_x^2-k_y^2-\lambda_0^{-}2}\right]\ , \tag{2.5}$$

where $k'=\sqrt{k_y^2+\lambda_0^{-2}}$. Integrals over k_x give modified Bessel functions [16]

$$V(r)=\frac{4q^2\lambda_0^2}{\pi|x|}\left[\int_0^\infty dk_y\cos(k_y y)\left[k_y K_1(k_y|x|)-\sqrt{k_y^2+\lambda_0^{-2}}K_1\left(|x|\sqrt{k_y^2+\lambda_0^{-2}}\right)\right]\right]\ . \tag{2.6}$$

According to general formulas of Bessel function integrals [16], the integrals over k_y can be calculated exactly. The results is

$$V(r)=\frac{2q^2\lambda_0^2}{r^3}\left[1-\left[1+\frac{r}{\lambda_0}\right]e^{-r/\lambda_0}\right]$$

$$\simeq\begin{cases}\dfrac{q^2}{r}, & r\ll\lambda_0\\[2ex] \dfrac{2q^2\lambda_0^2}{r^3}, & \lambda_0\ll r\ .\end{cases} \tag{2.7}$$

As follows from Eq. (2.7), with a long distance the interaction potential decreases as $1/r^3$, which is faster than in the pure vacuum interaction $(1/r)$ but slower than in the pure electrolyte $[(1/r)e^{-r/\lambda_0}]$.

(ii) Colloidal particles in a thin film of the electrolyte. This case corresponds to small d in Eq. (2.2). Putting also $z=u=0$ and taking into account that for a thin film the wave vector scales as $k\sim d/\lambda_0^2$ and hence $k\lambda_0\ll 1$, one can obtain from Eq. (2.2)

$$V(r)=2\pi q^2\int\frac{d^2k}{(2\pi)^2k}\frac{e^{i\vec{k}\cdot\vec{r}}}{k+\dfrac{d}{2\lambda_0^2}}$$

$$=q^2\int_0^\infty\frac{kdk}{k+\dfrac{d}{2\lambda_0^2}}J_0(kr)\ . \tag{2.8}$$

Using formulas for Bessel function integrals [16], one can transform Eq. (2.8) into the following:

$$V(r)=\frac{\pi q^2d}{4\lambda_0^2}\left[\frac{4\lambda_0^2}{\pi rd}-H_0\left[\frac{rd}{2\lambda_0^2}\right]+N_0\left[\frac{rd}{2\lambda_0^2}\right]\right]$$

$$\simeq\frac{q^2d}{2\lambda_0^2}\begin{cases}\dfrac{2\lambda_0^2}{rd}+\ln\left[\dfrac{2\lambda_0^2}{rd}\right], & r\ll\dfrac{\lambda_0^2}{d}\\[2ex] \left[\dfrac{2\lambda_0^2}{rd}\right]^3, & \dfrac{\lambda_0^2}{d}\ll r\ .\end{cases} \tag{2.9}$$

Here $H_0(z)$ is the Struve function and $N_0(z)$ is the Neuman function.

(iii) Colloidal particles in the center of the electrolyte film. In this case one should put $u=z=0$ into Eq. (2.2). Let us consider an important case of a thick film when $\lambda_0\ll d$. Then the interaction potential of two particles, placed in the middle of such a film, is

$$V(r)=2\pi q^2\int\frac{d^2k}{(2\pi)^2}\left[\frac{1}{k_0}+2\lambda^2\exp(-2dk_0)\times\left[\frac{2k^2+\lambda_0^{-2}}{k_0}-2k\right]\right]\ . \tag{2.10}$$

The first term in the right-hand side results in the conventional bulk interaction $(q^2/r)e^{-r/\lambda_0}$. The second term is proportional to $e^{-r^2/4d\lambda_0}$ and $k\lambda_0\ll 1$. To calculate this, one has to expand the exponent $2dk_0=2d/\lambda_0+k^2\lambda_0d$ and omit $k\lambda_0$ in other places. The third term in Eq. (2.10) can be written in the form, at $\sqrt{d\lambda_0}\ll r$,

$$\frac{2q^2\lambda_0^2}{\pi}e^{-2d/\lambda_0}\int_{-\infty}^{\infty}dk_ye^{ik_yy}\int_{|k_y|}^{\infty}dk_x\sqrt{k_x^2-k_y^2e^{-k_x|x|}}\ ,$$

which gives the r^{-3} part of the interaction potential. Collecting all three contributions in Eq. (2.10), one can obtain

$$V(r)=\frac{q^2}{r}e^{-r/\lambda_0}+\left[\frac{q^2}{d}e^{-r^2/4\lambda_0d}+\frac{2q^2\lambda_0^2}{r^3}\right]e^{-2d/\lambda_0}\ . \tag{2.11}$$

The third term in Eq. (2.11) is valid at $\sqrt{d\lambda_0}\ll r$. Compared with previous cases, the r^{-3} asymptotics is exponentially small since only a small fraction of the effective field penetrates the region outside the film. The first term in Eq. (11) is the conventional Yukawa potential. This is the main contribution to $V(r)$ for the sufficiently short distance (see also Ref. [17]). If r is larger or approximately equal to $2d$, the interaction becomes the r^{-3} type.

III. BUCKLING OF A COLLOIDAL CRYSTAL IN THE MIDDLE OF THE FILM

The most preferable position of a colloidal particle in the film is the middle. In this case the electrostatic energy $E^2/8\pi$ has its minimal value since the electric field in the film is better screened than in the vacuum. When the density of the colloidal particles is increased, they will collect in the middle plane of the flat film as soon as the concentration is less than some critical value. At bigger concentrations the effect of the interparticle repulsion becomes stronger than the repulsion between a particle and the film boundary. This results in the buckling of the particle system: one-half of the particles shifts up from the middle and the rest shifts down. This effect has been considered for vortices in a superconducting film [7]. See also [18]. Buckling of a crystal layer of colloidal particles was considered in Ref. [8]. The similar effect for the colloidal liquid is reported in Ref. [19].

In this section we consider the buckling of a crystal layer in the middle of the film of thickness $2d\gg\lambda_0$. Under this condition, as follows from Eq. (2.2), the electrostatic potential of the particle, shifted by the distance u from the middle of the film, is

$$\varphi_u(\vec{r},z)=\frac{q}{R}e^{-R/\lambda_0}+\frac{q}{d}e^{-2d/\lambda_0}\cosh\left[\frac{u+z}{\lambda_0}\right]\exp\left[-\frac{r^2}{4d\lambda_0}\right]\ , \tag{3.1}$$

with $R^2=r^2+z^2$ and $r^2=x^2+y^2$. This formula is just a generalization of Eq. (2.11) for finite u and z. We omitted the third term in Eq. (2.11).

Buckling of a hexagonal colloidal layer in the middle of the film can occur as shown in Fig. 2. The open (full) circle corresponds to a particle shifted up (down). The surface energy density E can be written in the form

$$E=\frac{2}{b^2\sqrt{3}}\sum_n q\varphi_u(\vec{r}_n,z_n)\ , \tag{3.2}$$

where $b^2\sqrt{3}/2$ is the unit cell area, $\vec{r}_n$ is the vector of the hexagonal lattice, and $z_n=\pm u$. The summation in Eq. (3.2) is extended over all particles, including $\vec{r}_n=0$. We have to extract only the u-dependent part δE of the energy density in Eq. (3.2). The first term of Eq. (3.1) contributes to δE if $\vec{r}_n$ connects open and full circles in Fig. 2(a). Since the interparticle distance under consideration b is bigger than the Debye-Hückel radius λ_0, one can consider only four nearest neighbors (full circles) of the central open circle in Fig. 2(a), i.e., $|\vec{r}_n|=b$.

The second term in Eq. (3.1) is important only for the self-energy when $\vec{r}_n=0$ and $z=u$. Writing $R_n\simeq b+2u^2/b$ and expanding the first term in Eq. (3.1) up to u^2, one can obtain the u-dependent part of the surface energy density

$$\delta E=\frac{2q^2}{b^2\sqrt{3}}\left[-\frac{8u^2}{\lambda_0 b^2}e^{-b/\lambda_0}+\frac{2}{d}e^{-2d/\lambda_0}\sinh^2\left[\frac{u}{\lambda_0}\right]\right]. \tag{3.3}$$

We chose the condition $\delta E(u=0)=0$. The buckling amplitude u has to be found out by the minimization of Eq. (3.3) with respect to u. The result is (Fig. 3)

$$\frac{\lambda_0}{2u}\sinh\left[\frac{2u}{\lambda_0}\right]=\frac{4\lambda_0 d}{b^2}e^{(2d-b)/\lambda_0}\ ,$$

$$u=\begin{cases}\left[3\lambda_0\left[d-\dfrac{b}{2}\right]\right]^{1/2}, & d-\dfrac{b}{2}\ll\lambda_0\\ d-\dfrac{b}{2}, & b\sim d\ .\end{cases} \tag{3.4}$$

The interparticle distance b is expressed through the surface density of particles n as $n=2/b^2\sqrt{3}$. We see that the critical concentration n_c for buckling is $n_c=1/2d^2\sqrt{3}$. For the bigger concentration (smaller b) the buckling amplitude u increases and distortions of other types (tripleting and so on) start to be involved in the formation of the three-dimensional colloidal crystal. For this reason, the high concentration part in Fig. 3 is shown by the dashed line. In this region the parameter u has rather the meaning of the domain size in z direction filled by the colloidal crystal.

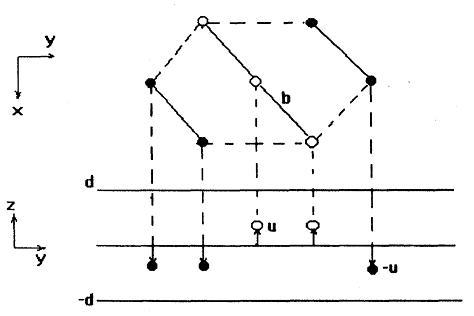

FIG. 2. (a) Buckling scheme of the colloidal crystal monolayer in the middle of the film; (b) motion of colloidal particles.

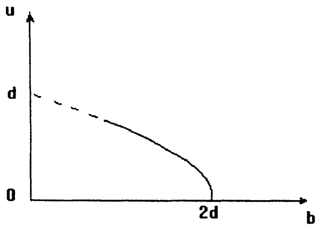

FIG. 3. Buckling amplitude as function of the interparticle distance b. At $(2d-b)\sim b$ (dashed line) the particle distribution becomes more complicated than a simple buckling.

IV. CRYSTALLIZATION OF A TWO-DIMENSIONAL COLLOIDAL LIQUID

The two-dimensional systems can be realized, for example, by colloidal particles on the interface between dielectric and electrolyte or in the middle of an electrolyte film. The crystallization condition of a two-dimensional liquid is easily formulated as the melting of a crystal phase. The two-dimensional crystal can be described in terms of elasticity theory. The elastic energy has the form [20]

$$E_{el}=\tfrac{1}{2}\int d^2r(2\mu u_{ik}^2+\lambda u_{ll}^2) \tag{4.1}$$

where $u_{ik}=\frac{1}{2}[\partial u_1/\partial r_k+\partial u_k/\partial r_i]$ is the strain tensor and μ and λ are Lame coefficients. According to Berezinskii [9] and Kosterlitz and Thouless [10], melting of the two-dimensional crystal occurs via the spontaneous thermal creation of edge dislocations. The condition for this can be written as $F=0$. The free energy F is given by [10]

$$F=E-TS_{\text{tr}}\ , \tag{4.2}$$

where

$$E=\frac{b^2}{2\pi}\mu\frac{\lambda+\mu}{\lambda+2\mu}\ln\left[\frac{R}{b}\right]$$

is the mean-field elastic energy of the edge dislocation, $S_{\text{tr}}=\ln(R^2/b^2)$ is the translational entropy of the dislocation, R is the system size, and b is the interparticle distance. The crystallization (melting) condition is

$$T_0=A\frac{b^2}{4\pi}\mu\frac{\lambda+\mu}{\lambda+2\mu}\ , \tag{4.3}$$

were the coefficient $A\simeq 0.65$ takes into account the screening effect of dislocations at the transition point [21].

Lame coefficients can be expressed through the shear modulus c_{66} and the compression one c_{11} as $\mu=c_{66}$ and $\lambda+2\mu=c_{11}$. We take the modulus notation that is appropriate for a hexagonal lattice. If the interparticle interaction can be described by the isotropic pair potential $V(r)$, elastic moduli have the form [22]

$$\begin{aligned} c_{66}&=\frac{n}{16}\sum_{l}[r_l^2V''(r_l)+3r_lV'(r_l)] ,\\ c_{11}&=\frac{n}{16}\sum_{l}[3r_l^2V''(r_l)+r_lV'(r_l)] , \end{aligned} \tag{4.4}$$

where n is the two-dimensional particle density and summation goes over all crystal sites.

Let us consider first the melting condition for the two-dimensional colloidal crystal in the middle of a film studied in Sec. III. One can take only the first term in Eq. (2.11) as an interaction potential $V(r)=(q^2/r)e^{-r/\lambda_0}$. Substituting this potential into formulas (4.4) and taking into account only six nearest neighbors one can obtain for Lame coefficients

$$\mu=\lambda=\frac{\sqrt{3}}{4}\frac{q^2}{\lambda_0^2 b}e^{-b/\lambda_0} . \tag{4.5}$$

The crystallization condition (4.3) gives

$$T_0=\frac{A}{8\pi\sqrt{3}}\frac{q^2 b}{\lambda_0^2}e^{-b/\lambda_0} . \tag{4.6}$$

For applicability of the Debye-Hückle approximation [linear equation (2.1) for the electrostatic potential] the inequality $V(b)<T$ should hold. By means of Eq. (4.6), this condition can be written in the form

$$\frac{V(b)}{T}=\frac{8\pi\sqrt{3}}{A}\left[\frac{\lambda_0}{b}\right]^2\frac{T_0}{T}<1 . \tag{4.7}$$

In our case, $\lambda_0 \ll b$, and we can consider a temperature that is much less than the melting temperature T_0.

One has to mention here that consideration of the buckling within the mean-field approximation, supposed thermal fluctuations to be small. The amplitude δu of thermal fluctuation can be found from the condition

$$\frac{(\delta u)^2}{2}\frac{\partial^2}{\partial u^2}\left[\frac{b^2\sqrt{3}}{2}\delta E\right]\simeq T , \tag{4.8}$$

where δE is the surface energy density determined by Eq. (3.3). Using the formula (3.4) for the mean-field displacement u and the expression for the melting temperature (4.6), one can obtain from Eq. (4.8)

$$\left[\frac{\delta u}{u}\right]^2\simeq\frac{T}{T_0}\frac{A}{4\pi\sqrt{3}}\left[\frac{b}{\lambda_0}\right]^3\left[\frac{\lambda_0}{2u}\right]^2\frac{1}{\frac{2u}{\lambda_0}\coth\left[\frac{2u}{\lambda_0}\right]-1} < 1 . \tag{4.9}$$

This value should be small for the applicability of the mean-field results. One can see that, for thick films, $\lambda_0<d$, one can satisfy simultaneously three conditions: (i) $T<T_0$ (the existence of a two-dimensional colloidal crystal in the middle of the film), (ii) inequality (4.7) (the applicability of the Debye-Hückel approximation), and (iii) inequality (4.9) (the validity of the mean-field approximation for the buckling problem).

Let us consider now the crystallization of the colloidal liquid on the surface of the electrolyte A in Sec. II). One can distinguish two important limiting cases:

(i) $n\lambda_0^2 \ll 1$. The distance between particles $b=(2/n\sqrt{3})^{1/2}$ is high compared with the Debye-Hückel radius λ_0. In this case the interaction potential is $V=2q^2\lambda_0^2/r^3$, and according to Eqs. (4.4),

$$\begin{aligned} \mu&=\tfrac{1}{9}\lambda=2\pi\sqrt{3}c_1\frac{q^2}{\lambda_0^3}(n\lambda_0^2)^{5/2}\\ c_1&=\frac{3^{5/4}}{32\pi\sqrt{2}}\sum_{r_n\neq 0}\left[\frac{b}{r_n}\right]^3 . \end{aligned} \tag{4.10}$$

(ii) $1 \ll n\lambda_0^2$. In this case $V=q^2/r$ and

$$\begin{aligned} \mu&=2\pi\sqrt{3}c_2q^2n^{3/2} ,\\ \lambda&=4\pi n^2q^2\lambda_0^2\sim\frac{\lambda_0}{b}\mu\gg\mu ,\\ c_2&=\frac{1}{32\pi\sqrt{2}}\left[\sqrt{n}\int\frac{d^2r}{r}-\frac{1}{\sqrt{n}}\sum_{r_l\neq 0}\frac{1}{r_l}\right] . \end{aligned} \tag{4.11}$$

c_1 and c_2 are numerical constants and $\vec{r}_1$ is the vector of the hexagonal lattice. The constant c_2 is expressed through the convergent difference of the integration over all space and the lattice sum.

The melting temperature, defined by Eq. (4.3), satisfies the relations

$$\frac{T_0\lambda_0}{q^2}=\begin{cases} Ac_1(n\lambda_0^2)^{3/2}, & n\lambda_0^2\ll 1\\ Ac_2(n\lambda_0^2)^{1/2}, & 1\ll n\lambda_0^2 . \end{cases} \tag{4.12}$$

This dependence is shown schematically in Fig. 4. It should be noticed that the experimental dependence $T_0(n)$ in the limit of a small concentration can provide the information on the interaction potential. According to Eqs. (4.6) and (4.12), one can write the relations as

$$\left[V(r)\sim e^{-r/\lambda_0},\ \ T_0\sim\exp\left[-\left[\frac{2}{n\lambda_0^2\sqrt{3}}\right]^{1/2}\right]\right.$$
$$\left[V(r)\sim\frac{1}{r^{\nu}},\ \ T_0\sim n^{\nu/2}\right] . \tag{4.13}$$

So, the crystallization phase diagram supplements other

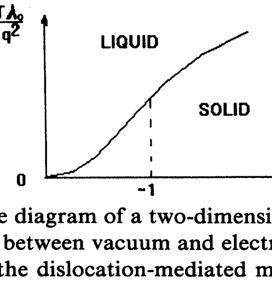

FIG. 4. Phase diagram of a two-dimensional colloidal system on the interface between vacuum and electrolyte. The solid line corresponds to the dislocation-mediated melting of a crystal to the hexatic liquid.

experimental methods of the investigation of the interaction between colloidal particles.

The charge of a colloidal particle is $q = Ne$, where e is the electron charge and N is a big number, $N \sim 10^2$. At room temperature

$$\frac{T_0\lambda_0}{q^2} \simeq \frac{\lambda_0(\mu m)}{N^2} . \tag{4.14}$$

The screening radius λ_0 is an experimentally controlled parameter that, in principle, enables us to sweep the melting curve (Fig. 4).

In the limit of low concentration, $n\lambda_0^2 \ll 1$, the interaction energy between two particles on the surface of the electrolyte $V(b) \sim T_0$; thus, considering the crystallization of a colloidal liquid, we are at the border of the applicability of the Debye-Hückel approximation. For high concentration $1 \ll n\lambda_0^2$ screening effects on the Lame coefficient, μ are not important and Eq. (2.1) holds.

The melting of a colloidal crystal, considered in this section, corresponds to the loss of translational order. The crystal goes over into the hexatic state, where the orientational order is conserved [11–13].

V. EFFECT OF THERMAL FLUCTUATIONS ON DISLOCATION-MEDIATED MELTING

In this section we consider the melting of two-dimensional crystals with exponential interparticle interaction $V(r) \sim \exp(-r/\lambda_0)$. The interparticle distance b is supposed to be larger than λ_0. As one can see from Eq. (4.7), at the melting temperature T_0, $V(b)/T_0 \sim (\lambda_0/b)^2 \ll 1$. This implies strong thermal fluctuations since the temperature is higher that the energy scale of the problem. In this case the approach, based upon the free energy of the edge dislocation (4.2), breaks down. The first term E in the free energy (4.2), which is the mean-field energy of the dislocation, should be modified to account for thermal fluctuations of particles in the field of the edge dislocation. The modified free energy has the form

$$F = E - TS_{\text{in}} - TS_{\text{tr}} , \tag{5.1}$$

where the translational entropy S_{tr} is due to translational degrees of freedom of the dislocation and has the same form as in Eq. (4.2). S_{in} accounts for inner degrees of freedom of the dislocation.

The analogous situation has been considered for another topological object: the vortex in a type 2 superconductor, where fluctuations of inner degrees of freedom play an important role [23]. Some consideration of inner fluctuations for an edge dislocation has been given in Ref. [13]. In this section we present the exact calculation of S_{in} up to zeroth order in $T/V(b)$.

The edge dislocation is described by the lattice displacement [20]

$$u_x = \frac{b}{2\pi}\left[\arctan\frac{y}{x} + \frac{\lambda+\mu}{\lambda+2\mu}\frac{xy}{x^2+y^2}\right] ,$$

$$u_y = -\frac{b}{2\pi}\left[\frac{\mu}{\lambda+2\mu}\ln\sqrt{x^2+y^2} + \frac{\lambda+\mu}{\lambda+2\mu}\frac{x^2}{x^2+y^2}\right] . \tag{5.2}$$

Then, as shown in the Appendix, the free energy of the edge dislocation has the form

$$F = \frac{b^2}{2\pi}\mu\frac{\lambda+\mu}{\lambda+2\mu}\ln\frac{R}{b} + \frac{T}{2\pi\sqrt{3}}\left[\frac{b}{3\lambda_0}\right]^2\left[\frac{\lambda+\mu}{\lambda+2\mu}\right]^2\ln\frac{R}{b} - TS_{\text{tr}} , \tag{5.3}$$

where the translational entropy S_{tr} has the same form as in Eq. (4.2) and Lame coefficients are

$$\mu = \lambda = \frac{\sqrt{3}}{4\lambda_0^2}V(b) . \tag{5.4}$$

The interaction potential between particles is supposed to be $V(r) \sim \exp(-r/\lambda_0)$. So, the entropy of the edge dislocation due to fluctuations of inner degrees of freedom can be obtained by comparing Eqs. (5.1) and (5.3):

$$S_{\text{in}} = -\frac{2}{\pi\sqrt{3}}\left[\frac{b}{9\lambda_0}\right]^2\ln\frac{R}{b} . \tag{5.5}$$

The negative sign of S_{in} is not in contradiction with thermodynamics, since S_{in} is just the difference between the positive entropy of the lattice with the dislocation and the positive entropy of the same lattice without the dislocation. S_{in} is negative, since the lattice, distorted by the edge dislocation, becomes stiffer with respect to the small oscillation of particles, and as a consequence, the lattice becomes less fluctuating, which decreases the inner entropy.

The free energy of the edge dislocation is

$$F = \frac{1}{4\pi\sqrt{3}}\left[\frac{b}{\lambda_0}\right]^2\left[V(b) + \frac{8}{81}T\right]\ln\frac{R}{b} - T\ln\frac{R^2}{b^2} . \tag{5.6}$$

The first term in brackets just corresponds to the mean-field energy E in Eq. (5.2). The second term in brackets is due to the inner entropy S_{in} in Eq. (5.1). Equation (5.6) is valid until $V(b) \gg \frac{8}{81}T$. One can see from Eq. (5.6) that the melting condition is given by the conventional formula (4.3) as soon as the particle concentration satisfies the condition

$$n\lambda_0^2 > \frac{2}{243\pi} \simeq 2.6\times 10^{-3} . \tag{5.7}$$

So, the numerical coefficient $\frac{8}{81}$ in Eq. (5.6) essentially reduces the importance of fluctuations. Nevertheless, for particle concentrations lower than that given by Eq. (5.7), one has to take into account all orders of the parameter $T/V(b)$ in the inner entropy S_{in}. This means that the system of particles with low concentration cannot be described in terms of the mean-field approach.

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APPENDIX

We derive here Eq. (5.3), where the second term accounts for the fluctuations of inner degrees of freedom of the edge dislocation. The lattice energy has the form [22]

$$\mathscr{E}=\tfrac{1}{2}\sum_{nm} V[\vec{r}_n-\vec{r}_m+\vec{u}_n-\vec{u}_m+\delta\vec{u}(\vec{r}_n+\vec{u}_n)-\delta\vec{u}(\vec{r}_m+\vec{u}_m)]-\tfrac{1}{2}\sum_{nm} V(\vec{r}_n-\vec{r}_m+\vec{u}_n-\vec{u}_m)\ . \tag{A1}$$

Here $\vec{r}_n$ is the vector of the lattice site, $\vec{u}_n$ is the dislocation field, and $\delta\vec{u}_n$ is a small lattice distortion. Making an expansion up to second order in δu and u and going over to the Fourier representation, one can obtain expression $\mathscr{E}=\mathscr{E}(1)$, where

$$\mathscr{E}(\nu)=\tfrac{1}{2}\int\frac{d^2q}{(2\pi)^2}\left[G_{ij}^{-1}(\vec{q})\delta u_i(\vec{q})\delta u_j(-\vec{q})+\nu\int\frac{d^2k}{(2\pi)^2}g_{ij}(\vec{q},\vec{k})\delta u_i(\vec{q})\delta u_j(-\vec{q}-\vec{k})\right]\ . \tag{A2}$$

The integration is taken over the Brillouin zone; the Green function is

$$G_{ij}^{-1}(\vec{q})=c_{11}q_iq_j+c_{66}(q^2\delta_{ij}-q_iq_j) \tag{A3}$$

and

$$g_{ij}(\vec{q},\vec{k})=\vec{q}_p(\vec{q}+\vec{k})_q\int d^2re^{-i\vec{k}\cdot\vec{r}}rT_{ij}^{pq}(\vec{r})\ , \tag{A4}$$

$$\begin{aligned}T_{ij}^{pq}(\vec{r})={}&\tfrac{1}{2}\Theta(x)\delta(y)\frac{\partial u_y(\vec{r})}{\partial x}\sum_{n_{ny}\neq 0} sgn(r_{ny})\frac{\partial}{\partial r_{ny}}f_{ij}^{pq}(\vec{r}_n)+\frac{1}{b^2\sqrt{3}}\frac{\partial u^{2k}(\vec{r})}{\partial r^s}\sum_{r_n} r_n^s\frac{\partial}{\partial r_n^k}f_{ij}^{pq}(\vec{r}_n)\\&+\frac{1}{2b^2\sqrt{3}}\frac{\partial u^k(\vec{r})}{\partial r^s}\frac{\partial u^l(\vec{r})}{\partial r^t}\sum_{r_n} r_n^sr_n^t\frac{\partial^2}{\partial r_n^k\partial r_n^l}f_{ij}^{pq}(\vec{r}_n)\ ,\end{aligned} \tag{A5}$$

$$f_{ij}^{pq}(\vec{r}_n)=r_n^pr_n^q\partial^2\partial r_n^i\partial r_n^j V(r_n)\ . \tag{A6}$$

The first term in Eq. (A5) corresponds to the topological property of the displacement $\vec{u}(\vec{r})$, namely, an increase of u_x+b after circulating around the singularity. The other two terms in Eq. (A5) are the same as for a nontopological (small) displacement.

The fluctuational part of the free energy (non–mean-field part) depends on g_{ij}, and the total free energy (we omit here the translational part) can be written in the form

$$F(\nu)=F(0)+F_1(\nu)=U-T\ln\int D\,\delta u\,\exp\left[-\frac{\mathscr{E}(\nu)}{T}\right]\ . \tag{A7}$$

U is the mean-field energy of the lattice with the dislocation and $F_1(\nu)=-TS_{\text{in}}$ is the part of the total free energy corresponding to fluctuations of inner degrees of freedom of the dislocation.

The path integration in Eq. (A7) is taken over δu. Differentiation of Eq. (A7) gives

$$\begin{aligned}\frac{\partial F_1(\nu)}{\partial\nu}={}&\frac{1}{\int D\delta u\,\exp[-\mathscr{E}(\nu)/T]}\\&\times\int D\delta u\left[\tfrac{1}{2}\int\frac{d^2q}{(2\pi)^2}\frac{d^2k}{(2\pi)^2}g_{ij}(\vec{q},\vec{k})\delta u_i(\vec{q})\delta u_j(-\vec{q}-\vec{k})\right]\exp[-\mathscr{E}(\nu)/T]\ .\end{aligned} \tag{A8}$$

The right-hand side of Eq. (7.8) can be written by means of Green's functions

$$\begin{aligned}\frac{\partial F_1(\nu)}{\partial\nu}={}&\frac{T}{2}\int\frac{d^2q}{(2\pi)^2}T_{ij}^{pq}(\vec{k}=0)q_pq_pG_{ij}(\vec{q})\\&-\frac{\nu T}{2}\int\frac{d^2q}{(2\pi)^2}\frac{d^2k}{(2\pi)^2}T_{ij}^{pq}(\vec{k})q_pq_{p_1}G_{ii_1}(\vec{q})T_{i_1j_1}^{p_1q_1}(-\vec{k})(\vec{q}+\vec{k})_{q_1}(\vec{q}+\vec{k})_qG_{jj}(\vec{q}+\vec{k})\ .\end{aligned} \tag{A9}$$

The mean-squared displacement of the fluctuating field δu is expressed through Green's function

$$\langle\delta u_i(\vec{q})\delta u_j(\vec{q}_1)\rangle=T(2\pi)^2\delta(\vec{q}+\vec{q}_1)G_{ij}(\vec{q})\ . \tag{A10}$$

Using the formula $F_1(1)=\int_0^1 d\nu[\partial F_1(\nu)]/\partial\nu$ and Eqs. (A9), (A5), (A6), (A2), one discovers that $F_1(1)$ is equal to the second term in Eq. (5.3).

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