MELTING OF TWO-DIMENSIONAL COLLOIDS IN A MAGNETIC FIELD

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Me gusta lo levemente dislocado. Por ejemplo, el comentario de Beau Brummell después de un accidente: "Lástima, era mi pierna favorita."

HUGO HIRIART, *Configuraciones, La Jornada Semanal, 4 de agosto de 1996.*

Prologue

For us, and for our tragedy,

Here stooping to your clemency,

We beg your hearing patiently.

[Exit]

Hamlet

Is this a prologue, or the posy of a ring?

Ophelia

'Tis brief, my lord.

Hamlet

As woman's love.

WILLIAM SHAKESPEARE, *Hamlet, Act III, scene ii.*

Abstract

Melting of a two-dimensional colloidal crystal is considered on the base of the concept of spontaneous thermal creation of dislocations. The melting condition strongly depends on the elastic moduli of the two-dimensional crystal. These moduli are calculated in the specific limit of a colloidal particle interaction dominated by the magnetic dipole-dipole potential induced by an applied magnetic field. The melting condition is obtained in terms of magnetic field, particle density, and temperature. The obtained theoretical functional dependence of the melting curve coincides with the experimental observation.

Contents

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Introduction

Colloidal systems have been a subject of an intense investigation during the last years [1]. One of the important aspects of colloids is melting of colloidal crystals, which has been observed experimentally [2]. The theoretical background of this phenomenon has been done by Kosterlitz and Thouless [3], who proposed that solid-liquid phase transition in a two-dimensional system is due to the spontaneous creation of edge dislocations. These dislocations destroy crystalline order. The reason for spontaneous creation of such dislocations is that the free energy becomes negative at $T > T_m$, where T_m is the melting temperature. Using linear theory of elasticity, one can show, that the free energy of a single dislocation depends logarithmically on the size of the crystal, determining, together with the entropic term, the critical temperature T_m at which dislocations are created.

The use of elasticity theory implies knowledge of elastic coefficients, which, in turn, depend on interparticle interaction potential. The interparticle interaction is a serious problem, and it was a subject of long-standing interest [4, 5]. However, some colloidal particles in an external magnetic field, acquire magnetic moment, and the interaction potential can be dominated by the dipole-dipole interaction, which can be tuned to exceed the Van der Walls and electrostatic interactions. Such a colloidal system has been realized experimentally [6], providing the unique possibility to describe this system exactly.

In the next chapters we derive the expressions for elastic moduli of a two-dimensional colloidal crystal, taking into account only the magnetic interaction between particles. We also find the melting condition of such a system as a function of temperature T, particle density n, and magnetic field B.

2

Ordering in two-dimensional systems

As will be seen, it is necessary to define orientational order to describe a phase that differs topologically from both solid and isotropic liquid phases. This phase has been called *hexatic*, and it is characterized by quasi-long-range orientational order but short-range transaltional order.

2.1   Translational and orientational order

Two-dimensional systems can be described by two kinds of ordering: translational and orientational. The correlation functions give a quantitative way to analyze order. In the case of translational order, the density-density correlation function is used:

$$g_G(r) = \left\langle e^{i\mathbf{G}\,[\mathbf{u}(r)-\mathbf{u}(0)]} \right\rangle, \qquad (2.1)$$

where $\mathbf{u}$ is the displacement from the equilibrium, and $\mathbf{G}$ is the reciprocal lattice vector. When particles of the crystal are located outside of the points of the lattice (defined by the vector $\mathbf{G}$), the correlation function is different from 1, and it is said that the translational order is destroyed. This is represented in Fig. 2.1(a)

On the other hand, when hexagons in a triangular lattice have different orientation than most of the other ones, it is said that orientational order is destroyed The way of measure this loss of order is by mean of the orientational correlation function $g_6(r)$:

$$g_6(r) = \left\langle e^{i6[\theta(r)-\theta(0)]} \right\rangle. \qquad (2.2)$$

Here, $\theta(r)$ is the angle between the x-axis and the vector that connect two neighbor particles of the crystal, as indicated in Fig. 2.1(b). As can be noted, when orientation is lost, translational order is diminished too.
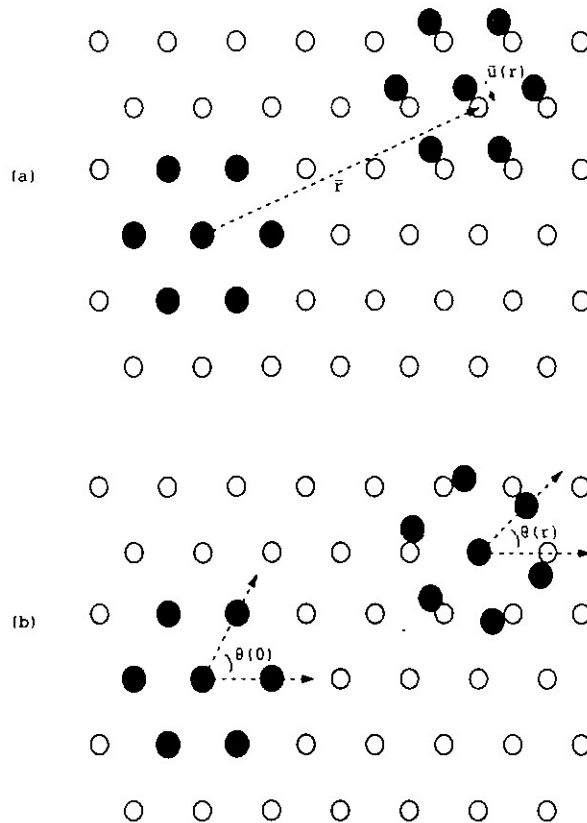
3

Figure 2.1: (a) Loss of translational order. (b) Loss of orientational order.

Although long-range translational order –this is, $g_G(r) = $ const– is impossible in two-dimensional colloids, a sort of *quasi-long-range order* is presented in the solid phase:

$$g_G(r) \propto \frac{1}{r^{\eta_G}} , \tag{2.3}$$

but long-range orientational order is present, i.e., $g_6(r) = $ const.

If the temperature in the crystal is augmented, thermal excitations can be strong enough to create topological defects in the lattice. When dislocations appears at a temperature T_m, translational order is lost, in the sense that the correlation function now decays rapidly:

$$g_G(r) \propto e^{-r/\xi_G} , \tag{2.4}$$

but orientational order still remains, since $g_6(r)$ now decays as $r^{-\eta_6}$. This is a BKT-type transition, after articles from Berezinskii [7] and Kosterlitz and Thouless [3], explaining the mechanism of this kind of continuous transitions in two-dimensional systems. Dislocations are characterized by the fact that, when a path around the dislocation is drawn, it fails to

close by certain amount, as can be seen in Fig. 2 2(a).

At $T = T_i$ greater than T_m, another BKT transition occurs via spontaneous creation of disclinations which destroys the orientational order:

$$g_6(r) \propto e^{-r/\xi_6} . \tag{2.5}$$

Disclinations can be viewed as points in the lattice that have an unusual number of neighbors. This is showed in Fig. 2.2(b). It can be noted that a dislocation in a hexagonal lattice is formed by the union of a five-fold and a seven-fold disclination.
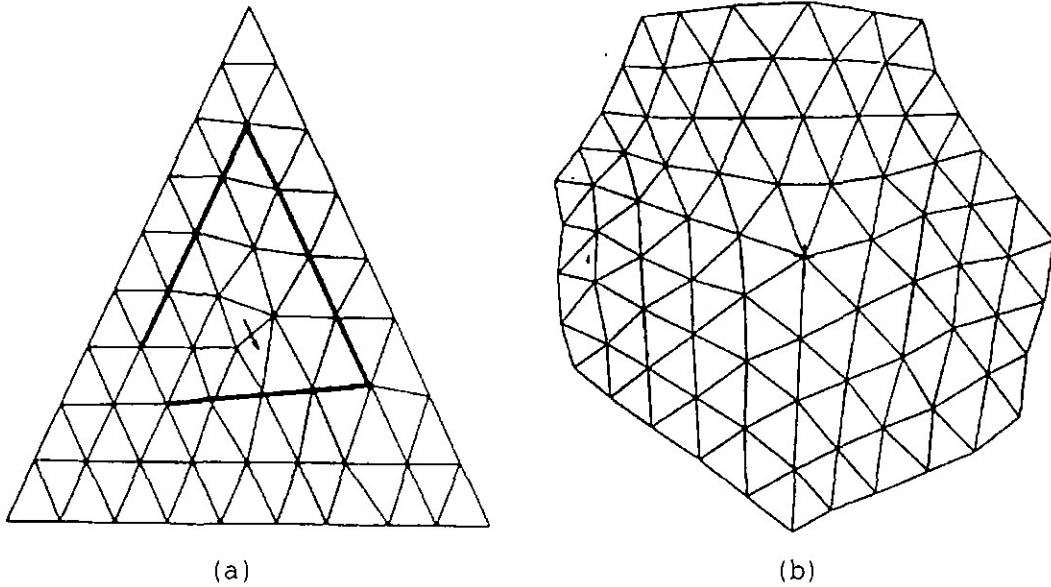

(a)   (b)

Figure 2.2: (a) Dislocation. (b) Disclination

This intermediate phase between order and disorder (i.e., between solid and isotropic fluid phases), exclusive of two-dimensional systems, is called *hexatic phase* due to the six-fold orientational order in hexagonal lattices.

2.2   Hexatic phases

Murray and Van Winkle [2] observed this hexatic phase in a two-dimensional colloidal suspension of charged particles, at fixed temperature but varying the particle density. The obtained images of the particles are shown in Fig. 2.3(a), as well as the computed structure factor and correlation function for each image. It is easy to note that, meanwhile density is decreased, translational order is lost before orientational order. The corresponding angular

averages of $g_G(r)$ and $g_6(r)$ are sketched in Fig. 2.3(b) (the labels b, d and f corresponds to the images in Fig. 2.3(a)). Note that small particle displacements are enough to take the system to the hexatic phase.

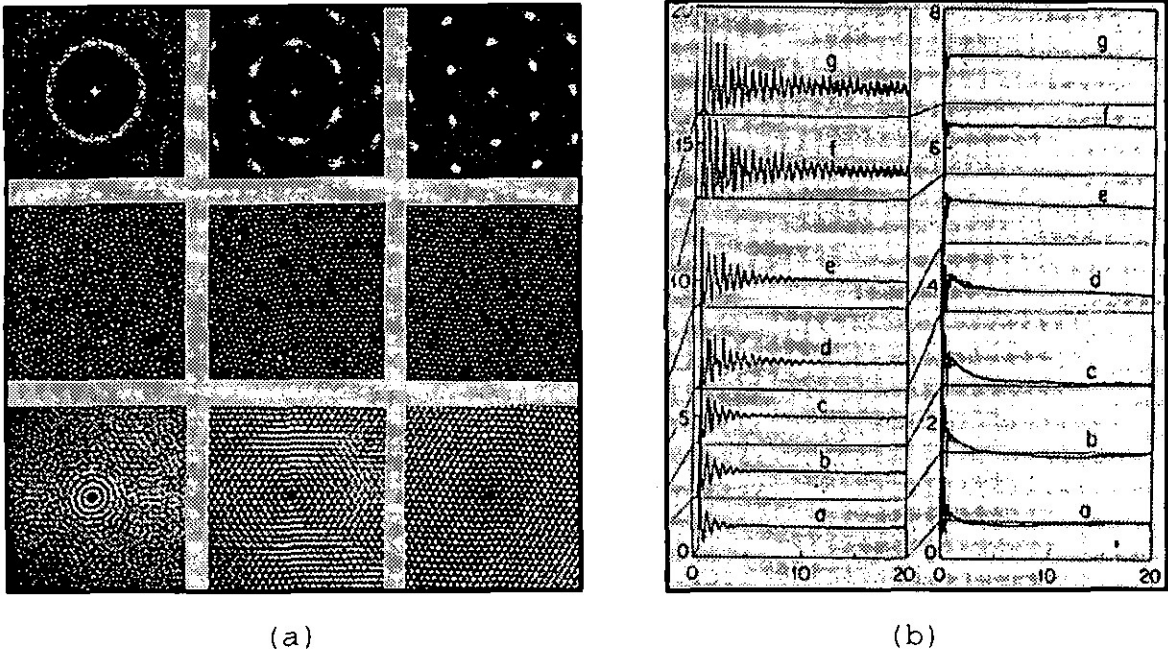(a)   (b)

Figure 2.3: (a) Top: $S(K)$; center: particles in the colloid; bottom: $g_G(r)$. Density increases from left to right. (b) Angular averages of $g_G(r)$ (left column) and $g_6(r)$ (right column). Density is higher at top. From Ref. [2].

Unlike the solid phase, in the hexatic phase the system does not react to shear, as a direct consequence of the absence of translational order. On the other hand, the hexatic liquid reacts to twist, differing in this with the isotropic, no orientational ordered liquid phase. These differences are included in Table 2.1, as well as the expressions for both translational and orientational correlation functions.

In the next chapters we will consider the solid–to–hexatic phase transition, since current experiments [6] involve a transition of this kind. To do this, elasticity theory will be used, since the energy associated to a dislocation depends on the elastic modulus of the system.

	T_m	T_i
crystal	hexatic liquid	isotropic liquid
power law translational order $g_G(r) \propto \frac{1}{r^{\eta_G}}$	no long range translational order $g_G(r) \propto e^{-r/\xi_G}$	no long range translational order $g_G(r) \propto e^{-r/\xi_G}$
long range orientational order $g_6(r) \propto const$	power law orientational order $g_6(r) \propto \frac{1}{r^{\eta_6}}$	no long range orientational order $g_G(r) \propto e^{-r/\xi_6}$
reaction on both shear and twist	reaction on twist	no reaction on both shear and twist

Table 2.1.

3

Elasticity theory

3.1   Strain and stress tensors

The displacement of a point in a body, due to a deformation, is given by the displacement vector $\mathbf{U}$:

$$U_i = X_i' - X_i \, , \tag{3.1}$$

where $\mathbf{X}$ and $\mathbf{X}'$ are the original and final position vectors of the point, respectively.

The distance between two nearest points, dl, is given by

$$dl^2 = dX_i^2 \, , \tag{3.2}$$

before the deformation, and by

$$dl'^2 = dX_i'^2 \, , \tag{3.3}$$

after the deformation (we are considering here the summation rule).

If

$$dU_i = \frac{\partial U_i}{\partial X_k} \, dX_k \, , \tag{3.4}$$

$$dl'^2 = dl^2 + 2 \frac{\partial U_i}{\partial X_k} \, dX_i \, dX_k + \frac{\partial U_i}{\partial X_k} \frac{\partial U_i}{\partial X_l} \, dX_k \, dX_l \, ,$$

but

$$2\frac{\partial U_i}{\partial X_k} = \left(\frac{\partial U_i}{\partial X_k} + \frac{\partial U_k}{\partial X_i} \right) \, , \tag{3.5}$$

and

$$\frac{\partial U_i}{\partial X_k}\frac{\partial U_i}{\partial X_l}\,dX_k\,dX_l = \frac{\partial U_l}{\partial X_i}\frac{\partial U_l}{\partial X_k}\,dX_i\,dX_k\,, \tag{3.6}$$

and then,

$$dl'^2 = dl^2 + 2U_{ik}\,dX_i\,dX_k \tag{3 7}$$

where we present the *strain tensor* [8]

$$U_{ik} = \frac{1}{2}\left(\frac{\partial U_i}{\partial X_k} + \frac{\partial U_k}{\partial X_i}\right) + \frac{\partial U_l}{\partial X_i}\frac{\partial U_l}{\partial X_k}\,. \tag{3.8}$$

For small deformations the derivatives are small too, and then we can write

$$U_{ik} = \frac{1}{2}\left(\frac{\partial U_i}{\partial X_k} + \frac{\partial U_k}{\partial X_i}\right); \tag{3.9}$$

this is the expression for the strain tensor that we are going to use in the rest of the treatment. From (3.7), we see that, if U_{ik} is diagonal, its principal values represents the relative extensions of the elements of length along the principal axis.

Let $\int \mathbf{F}\,dV$ be the total force on some portion of a body. Each $\int F_i\,dV$ can be transformed into an integral over the surface of this portion. Then, the vector F_i must be the divergence of a tensor of rank two·

$$F_i = \frac{\partial \sigma_{ik}}{\partial X_k}\,. \tag{3.10}$$

σ_{ik} is called *stress tensor* In this way,

$$\int F_i\,dV = \int \frac{\partial \sigma_{ik}}{\partial X_k}\,dV = \oint \sigma_{ik}\,df_k\,. \tag{3.11}$$

where $\sigma_{ik}\,df_k$ is the i-th component of the force acting on the surface element df, as illustrated in Fig. 3.1

The work done on the body by the internal stresses, changing U_i by a small amount δU_i, is given by

$$\int \delta R\,dV = \int \left(\frac{\partial \sigma_{ik}}{\partial X_k}\right)\delta U_i\,dV = \oint \sigma_{ik}\delta U_i\,df_k - \int \sigma_{ik}\frac{\partial \delta U_i}{\partial X_k}\,dV \tag{3.12}$$

In an infinite volume, $\sigma_{ik} = 0$ at the surface, and then,

$$\int \delta R\,dV = -\int \sigma_{ik}\frac{\partial \delta U_i}{\partial X_k}\,dV = -\frac{1}{2}\int \sigma_{ik}\left(\frac{\partial \delta U_i}{\partial X_k} + \frac{\partial \delta U_k}{\partial X_i}\right)dV\,, \tag{3.13}$$

$$\int \delta R\,dV = -\sigma_{ik}\int \delta U_{ik}\,dV\,,$$
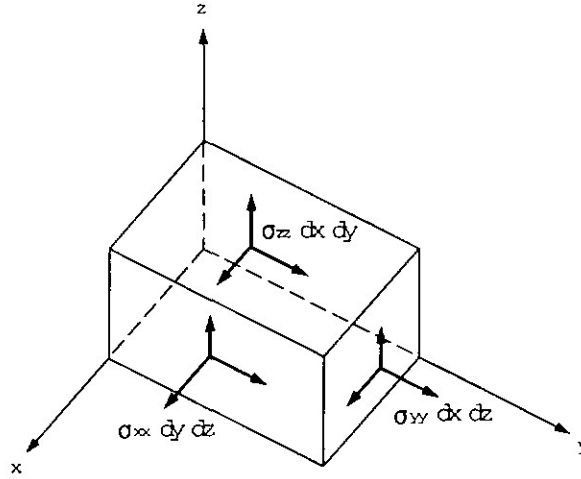
Figure 3.1: In a rectangular volume element $dx\,dy\,dz$, the stresses σ_{xx}, σ_{yy} and σ_{zz} are the forces per unit area.

so

$$\delta R = -\sigma_{ik}\delta U_{ik}\,. \tag{3.14}$$

For a reversible process, the internal energy is given by

$$dE = T\,dS - dR = T\,dS + \sigma_{ik}\,dU_{ik}\,, \tag{3.15}$$

and, since the Helmholtz free energy per volume unit is $F = E - TS$, then

$$dF = -S\,dT + \sigma_{ik}\,dU_{ik}\,, \tag{3.16}$$

and

$$\sigma_{ik} = \left(\frac{\partial F}{\partial U_{ik}}\right)_{T}\,. \tag{3.17}$$

3.2   The elastic moduli

Let us consider a slightly deformed body, at a temperature that remains constant throughout it. Then, we can expand F near $U_{ik} = 0$. But, since when $U_{ik} = 0$, $\sigma_{ik} = 0$ too, and $\sigma_{ik} = \frac{\partial F}{\partial U_{ik}}$, then there is no linear term, and F takes the general form (at second order)

$$F = \frac{1}{2}\int \lambda_{iklm}U_{ik}U_{lm}\,dx\,dy = \frac{1}{2}\int C_{\alpha\beta}U_{\alpha}U_{\beta}\,dx\,dy\,. \tag{3.18}$$

The fact that $\sigma_{ik} = \lambda_{iklm}U_{lm}$, this is, that the strain is proportional to the stress, is just the generalized form of the Hooke's Law. λ_{iklm} is a fourth-rank tensor –the *elastic tensor*–, and its components are known as *elastic moduli*.

For a hexagonal system, we take the sixth-order axis as the z-axis, and use the coordinates $\xi = x + iy$, and $\eta = x - iy$. In a rotation through $\frac{\pi}{3}$, $\xi \to \xi e^{i\frac{\pi}{3}}$, and $\eta \to \eta e^{-i\frac{\pi}{3}}$. By symmetry, only those components λ_{iklm} which are unchanged after this rotation can be different from zero, this is, only those which contains the same number of suffixes ξ and η, since $e^{i\frac{\pi}{3}}e^{-i\frac{\pi}{3}} = 1$. The energy is [8]

$$F = \frac{1}{2} \int (\lambda_{\xi\eta\xi\eta}U_{\xi\eta}^2 + \lambda_{\eta\xi\eta\xi}U_{\eta\xi}^2 + \lambda_{\xi\eta\eta\xi}U_{\xi\eta}U_{\eta\xi} + \lambda_{\eta\xi\xi\eta}U_{\eta\xi}U_{\xi\eta} + \lambda_{\xi\xi\eta\eta}U_{\xi\xi}U_{\eta\eta} \tag{3.19}$$
$$+ \lambda_{\eta\eta\xi\xi}U_{\eta\eta}U_{\xi\xi}) \, dx \, dy \, ,$$

but, since $U_{\eta\xi} = U_{\xi\eta}$, then $\lambda_{\xi\eta\xi\eta} = \lambda_{\eta\xi\eta\xi} = \lambda_{\xi\eta\eta\xi} = \lambda_{\eta\xi\xi\eta}$; and $\lambda_{\xi\xi\eta\eta} = \lambda_{\eta\eta\xi\xi}$. In this way

$$F = \int \left(2\lambda_{\xi\eta\xi\eta}U_{\xi\eta}^2 + \lambda_{\xi\xi\eta\eta}U_{\xi\xi}U_{\eta\eta} \right) dx \, dy \, . \tag{3.20}$$

In terms of the coordinates x, y:

$$\xi^2 = (x + iy)^2 = x^2 + y^2 + 2ixy \quad \Longrightarrow \quad U_{\xi\xi} = U_{xx} + U_{yy} + 2iU_{xy}; \tag{3.21}$$
$$\eta^2 = (x - iy)^2 = x^2 + y^2 - 2ixy \quad \Longrightarrow \quad U_{\eta\eta} = U_{xx} + U_{yy} - 2iU_{xy};$$
$$\xi\eta = (x + iy)(x - iy) = x^2 + y^2 \quad \Longrightarrow \quad U_{\xi\eta} = U_{xx} + U_{yy};$$

in such a way that we obtain that

$$U_{\xi\xi}U_{\eta\eta} = (U_{xx} - U_{yy})^2 + 4U_{xy}^2 \, , \tag{3.22}$$
$$U_{\xi\eta}^2 = (U_{xx} + U_{yy})^2 \, ,$$

and then,

$$F = \int \left[2\lambda_{\xi\eta\xi\eta}(U_{xx} + U_{yy})^2 + \lambda_{\xi\xi\eta\eta}\left((U_{xx} - U_{yy})^2 + 4U_{xy}^2\right) \right] dx \, dy \, . \tag{3.23}$$

To express the elastic moduli λ_{iklm} in the coordinates x, y, we must note that

$$\lambda_{xxxx} = 4\lambda_{\xi\eta\xi\eta} + 2\lambda_{\xi\xi\eta\eta} \, , \tag{3.24}$$
$$\lambda_{xyxy} = 2\lambda_{\xi\xi\eta\eta} \, ,$$

and then the free energy in terms of the elastic moduli λ_{xxxx} and λ_{xyxy} is

$$F = \frac{1}{2} \int \left[(\lambda_{xxxx} - \lambda_{xyxy})(U_{xx} + U_{yy})^2 + \lambda_{xyxy} \left((U_{xx} - U_{yy})^2 + 4U_{xy}^2 \right) \right] \, dx \, dy. \quad (3.25)$$

Making $\lambda_{xxxx} = C_{11}$, $\lambda_{xyxy} = C_{66}$, and using the fact that $U_{ik} = \frac{1}{2}(\frac{\partial U_i}{\partial X_k} + \frac{\partial U_k}{\partial X_i})$, then the expression for the free energy is

$$F = \frac{1}{2} \int \left[C_{11} \left(\frac{\partial U_x}{\partial x} + \frac{\partial U_y}{\partial y} \right)^2 + C_{66} \left(\frac{\partial U_x}{\partial y} - \frac{\partial U_y}{\partial x} \right)^2 + 4C_{66} \left(\frac{\partial U_x}{\partial y} \frac{\partial U_y}{\partial x} - \frac{\partial U_x}{\partial x} \frac{\partial U_y}{\partial y} \right) \right] \, dx \, dy .$$
$$(3.26)$$

C_{11} is called the *compression modulus*, since the first element on the right of (3.26) represents an increment of F due to a change of area (not shape), this is, a hydrostatic compression. Similarly, C_{66} is called the *shear modulus*, since the second term in (3.26) represents a pure shear, change in shape without alteration of volume.

3.3 The equations of equilibrium

In a state of thermodynamic equilibrium, the energy F is at a minimum, so the conditions to fulfill by the system are

$$\frac{\partial F}{\partial U_x} = 0, \quad \frac{\partial F}{\partial U_y} = 0, \quad (3.27)$$

where F is given by (3.26). From the first condition,

$$C_{11} \frac{\partial^2 U_x}{\partial x^2} + C_{11} \frac{\partial^2 U_y}{\partial x \partial y} + C_{66} \frac{\partial^2 U_x}{\partial y^2} - C_{66} \frac{\partial^2 U_y}{\partial x \partial y} = 0, \quad (3.28)$$

and from the second,

$$C_{11} \frac{\partial^2 U_y}{\partial y^2} + C_{11} \frac{\partial^2 U_x}{\partial x \partial y} - C_{66} \frac{\partial^2 U_x}{\partial y \partial x} + C_{66} \frac{\partial^2 U_y}{\partial x \partial y} = 0 \quad (3.29)$$

(note that, in absence of dislocations, the third element on the integral have no effect at all, since the derivatives cancels mutually).

Dividing $\frac{\partial F}{\partial U_i}$ by $2C_{66}$ and using the strain tensor, we have

$$\frac{\partial U_{xx}}{\partial x} + \frac{\partial U_{xy}}{\partial y} + \left(\frac{1}{2} \frac{C_{11}}{C_{66}} - 1 \right) \left(\frac{\partial U_{xx}}{\partial x} + \frac{\partial U_{yy}}{\partial x} \right) = 0, \quad (3.30)$$

$$\frac{\partial U_{yx}}{\partial x} + \frac{\partial U_{yy}}{\partial y} + \left(\frac{1}{2} \frac{C_{11}}{C_{66}} - 1 \right) \left(\frac{\partial U_{xx}}{\partial y} + \frac{\partial U_{yy}}{\partial y} \right) = 0.$$

This two conditions can be putted in the following way.

$$\frac{\partial U_{ik}}{\partial X_k} + \left(\frac{1}{2}\frac{C_{11}}{C_{66}} - 1\right)\frac{\partial U_{ll}}{\partial X_i} = 0. \tag{3.31}$$

This is the form of the conditions of equilibrium to use in our treatment of isolated dislocations in the crystal, as will be shown in the next section

3.4   The effect of an edge dislocation

Consider an edge dislocation on the lattice, as indicated in the Fig 3.2. The energy associated to this dislocation is determined by the form of the vector field $\mathbf{U}(\mathbf{X})$.
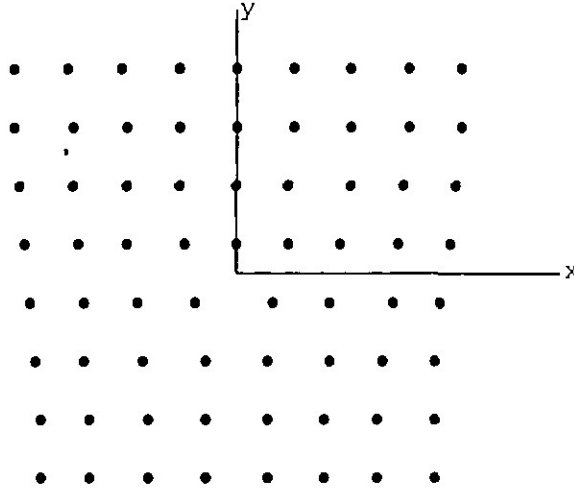

Figure 3.2: Edge dislocation located at the origin of coordinates. The displacement vector increments a vector **b**, equal to one lattice vector in magnitude and direction.

The displacement vector **U** seems incremented by a Burgers vector **b**, were b is the lattice parameter. This can be expressed as [8]

$$\oint_L dU_i = \oint \frac{\partial U_i}{\partial X_k}\, dX_k = -b_i. \tag{3.32}$$

Specifically, in our problem,

$$\oint_L dU_x = \oint \frac{\partial U_x}{\partial X_k}\, dX_k = -b_x, \qquad (b_y = b_z = 0). \tag{3.33}$$

According to Stokes' theorem

$$\oint \left[L\left(x,y\right) dx + M\left(x,y\right) dy \right] = \int \int_{S_L} \left(\frac{\partial M}{\partial x} - \frac{\partial L}{\partial y} \right) dx\, dy \,, \tag{3.34}$$

$$\oint \left[\frac{\partial U_x}{\partial x} dx + \frac{\partial U_x}{\partial y} dy \right] = \int \int_{S_L} \left[\frac{\partial}{\partial x} \left(\frac{\partial U_x}{\partial y} \right) - \frac{\partial}{\partial y} \left(\frac{\partial U_x}{\partial x} \right) \right] dx\, dy = -b_x \,.$$

This integral is zero, except in the origin, the point associated to the dislocation. From the definition of the two-dimensional *delta function*

$$\int \delta(\xi) \vec{\tau} \cdot d\mathbf{f} = \tau_i \int_{S_L} \delta(\xi)\, df_i = 1 \,. \tag{3.35}$$

Here $\vec{\tau}$ and $\mathbf{f}$ points to z, so,

$$\tau_z \int_{S_L} \delta(\xi)\, dx\, dy = 1 \,, \tag{3.36}$$

and then

$$\frac{\partial^2 U_x}{\partial x \partial y} - \frac{\partial^2 U_x}{\partial y \partial x} = -\tau_z \delta(\xi) b_x \,. \tag{3.37}$$

Defining the *distortion tensor*, W_{ik} :

$$W_{ik} = \frac{\partial U_k}{\partial X_i} \,, \tag{3.38}$$

and using the ϵ_{ilm} tensor, we can put this equation as

$$\epsilon_{ilm} \frac{\partial W_{mk}}{\partial X_l} = -\tau_i b_k \delta(\xi) \,, \qquad i,k,l,m : \{1,2,3\} \,. \tag{3.39}$$

Multiplying this by ϵ_{ikn} :

$$\epsilon_{ilm}\epsilon_{ikn} \frac{\partial W_{mk}}{\partial X_l} = -\epsilon_{ikn}\tau_i b_k \delta(\xi) \tag{3.40}$$

$$\epsilon_{ilm}\epsilon_{ikn} \frac{\partial W_{mk}}{\partial X_l} = (\delta_{lk}\delta_{nm} - \delta_{ln}\delta_{mk}) \frac{\partial W_{mk}}{\partial X_l} = -(\vec{\tau} \times \mathbf{b})_n \delta(\xi).$$

Writing the equations of equilibrium

$$\frac{\partial U_{ik}}{\partial X_k} + \left(\frac{1}{2}\frac{C_{11}}{C_{66}} - 1 \right) \frac{\partial U_{ll}}{\partial X_i} = 0 \tag{3.41}$$

in terms of the distortion tensor:

$$\frac{\partial}{\partial X_k} \left(\frac{1}{2} W_{ik} + \frac{1}{2} W_{ki} \right) + \left(\frac{1}{2} \frac{C_{11}}{C_{66}} - 1 \right) \frac{\partial W_{ll}}{\partial X_i} = 0 \tag{3.42}$$

$$\frac{\partial W_{ki}}{\partial X_k} + \left(\frac{C_{11}}{C_{66}} - 1 \right) \frac{\partial W_{ll}}{\partial X_i} = (\vec{\tau} \times \mathbf{b})_i \delta(\xi),$$

and, returning this expression to its dependence on U_i:

$$\frac{\partial^2 U_i}{\partial X_k} + \left(\frac{C_{11}}{C_{66}} - 1 \right) \frac{\partial}{\partial X_i} \left(\frac{\partial U_l}{\partial X_l} \right) = (\vec{\tau} \times \mathbf{b})_i \delta(\xi). \tag{3.43}$$

Here, $\frac{\partial^2 U_i}{\partial X_k}$ are the components of the vector $\triangle \mathbf{U}$, and $\frac{\partial}{\partial X_i}(\frac{\partial U_l}{\partial X_l})$ are the components of the vector $\nabla \times \nabla \cdot \mathbf{U}$. Then, putting this in terms of the vector $\mathbf{U}$:

$$\triangle \mathbf{U} + \left(\frac{C_{11}}{C_{66}} - 1 \right) \nabla \times \nabla \cdot \mathbf{U} = (\vec{\tau} \times \mathbf{b}) \delta(\xi). \tag{3.44}$$

Since $\vec{\tau}$ points to $-z$, and $\mathbf{b} = b_x i$ points to x:

$$\triangle \mathbf{U} + \left(\frac{C_{11}}{C_{66}} - 1 \right) \nabla \times \nabla \cdot \mathbf{U} = -b\hat{j}\delta(r) \tag{3.45}$$

(r lies on the xy-plane). The solution of equation (3.45) describes the displacement of the points of the lattice from their equilibrium positions, including the effect of the dislocation. To solve this equation, we must to seek a solution of type $\mathbf{U} = \mathbf{U_0} + \mathbf{U_1}$, where $\mathbf{U_1}$ is monovaluated, and $\mathbf{U_0}$ satisfies the equation (3.32). To choose $\mathbf{U_0}$, we can make use of the residue theorem $\oint_C f(z)\,dz = 2\pi i \mathrm{Res} f(a)$. Consider the integral $\oint df = \oint \frac{df}{dz}\,dz$. If $f(z) = \frac{b}{2\pi} \ln z$, then

$$\oint df(z) = \oint (\frac{df}{dz})\,dz = \oint \frac{b}{2\pi z}\,dz = 2\pi i \left(\frac{b}{2\pi} \right) = ib. \tag{3.46}$$

This is, $U_x^{(0)} = \Im(f)$ and $U_y^{(0)} = \Re(f)$ satisfies (3.32). Explicitly,

$$U_x^{(0)} = \frac{b\phi}{2\pi} \quad U_y^{(0)} = \frac{b}{2\pi} \ln r. \tag{3.47}$$

Since $\nabla \cdot \mathbf{U}^{(0)} = 0$, and $\triangle \mathbf{U}^{(0)} = b\hat{j}\delta(r)$, it follows that

$$\triangle \mathbf{U}^{(1)} + \left(\frac{C_{11}}{C_{66}} - 1 \right) \nabla \times \nabla \cdot \mathbf{U} = -b\hat{j}\delta(r)\mathbf{U}^{(1)} = -2b\hat{j}\delta(r). \tag{3.48}$$

This is the same problem of that of determine the deformation of equilibrium of an infinite elastic medium under forces concentrated along the z axis, with volume density $Eb\hat{j}\delta(r)[\frac{C_{11}-C_{66}}{3C_{11}-4C_{66}}]$ [8]. Thus,

$$\mathbf{U}^{(1)} = \frac{b}{4\pi}\left(1 - \frac{C_{66}}{C_{11}}\right) \cdot 2 \int_0^\infty \left[\left(\frac{C_{11} + C_{66}}{C_{11} - C_{66}}\right)\frac{\hat{\jmath}}{R} + \frac{\hat{r}y}{R^3}\right] dz' , \tag{3.49}$$

$$R = \sqrt{r^2 + z'^2} , \tag{3.50}$$

giving the result of

$$U_x = \frac{b}{2\pi}\left[\arctan\frac{y}{x} + \left(1 - \frac{C_{66}}{C_{11}}\right)\frac{xy}{x^2 + y^2}\right] \tag{3.51}$$

$$U_y = -\frac{b}{2\pi}\left[\frac{C_{66}}{C_{11}}\ln\sqrt{x^2 + y^2} + \left(1 - \frac{C_{66}}{C_{11}}\right)\frac{x^2}{x^2 + y^2}\right] \tag{3.52}$$

To evaluate the integral that appears in (3.26), that gives the value of the free energy of the crystal, we need the following derivatives:

$$\frac{\partial U_x}{\partial x} = \frac{b}{2\pi}\frac{y}{x^2 + y^2}\left(-\frac{2x^2}{x^2 + y^2} + \frac{C_{66}}{C_{11}}\frac{x^2 - y^2}{x^2 + y^2}\right) , \tag{3.53}$$

$$\frac{\partial U_y}{\partial y} = \frac{b}{2\pi}\frac{y}{x^2 + y^2}\left(\frac{2x^2}{x^2 + y^2} + \frac{C_{66}}{C_{11}}\frac{3x^2 + y^2}{x^2 + y^2}\right) , \tag{3.54}$$

$$\frac{\partial U_x}{\partial y} = \frac{b}{2\pi}\frac{x}{x^2 + y^2}\left(\frac{2x^2}{x^2 + y^2} + \frac{C_{66}}{C_{11}}\frac{y^2 - x^2}{x^2 + y^2}\right) , \tag{3.55}$$

$$\frac{\partial U_y}{\partial x} = \frac{b}{2\pi}\frac{x}{x^2 + y^2}\left(-\frac{2y^2}{x^2 + y^2} + \frac{C_{66}}{C_{11}}\frac{y^2 - x^2}{x^2 + y^2}\right) , \tag{3.56}$$

and then the expression for the free energy is equal to

$$F = \frac{1}{2}\frac{b^2}{4\pi^2}\int\left[C_{11}\frac{4y^2}{r^4}\frac{C_{66}^2}{C_{11}^2} + C_{66}\frac{4x^2}{r^4} + 4C_{66}\left(\frac{x^2}{r^4}\left(\frac{2x^2}{r^2} + \frac{C_{66}}{C_{11}}\frac{y^2 - x^2}{r^2}\right)\left(\frac{-2y^2}{r^2} + \frac{C_{66}}{C_{11}}\frac{y^2 - x^2}{r^2}\right)\right. \right. \tag{3.57}$$
$$\left.\left. - \frac{y^2}{r^4}\left(\frac{-2x^2}{r^2} + \frac{C_{66}}{C_{11}}\frac{x^2 - y^2}{r^2}\right)\left(\frac{2x^2}{r^2} - \frac{C_{66}}{C_{11}}\frac{3x^2 + y^2}{r^2}\right)\right)\right] dx\,dy ,$$

where $r^2 = x^2 + y^2$.

After some of algebra, all this reduces to

$$F = \frac{b^2}{2\pi^2}C_{66}\int\frac{1}{r^2}[\frac{C_{66}}{C_{11}}\frac{y^2}{r^2} + \frac{x^2}{r^2} - \frac{C_{66}}{C_{11}}\frac{2x^2}{r^2} + \frac{C_{66}^2}{C_{11}^2}\frac{x^2 - y^2}{r^2}]dxdy , \tag{3.58}$$

that, in polar coordinates, gives

$$F = \frac{b^2}{2\pi^2} C_{66} \int_{a_0}^{R} \frac{dr}{r} \cdot 2\pi \left(\frac{C_{66}}{C_{11}} \langle \sin^2 \phi \rangle + \langle \cos^2 \phi \rangle - 2\frac{C_{66}}{C_{11}} \langle \cos^2 \phi \rangle + \frac{C_{66}^2}{C_{11}^2} \langle \cos^2 \phi \rangle - \frac{C_{66}^2}{C_{11}^2} \langle \sin^2 \phi \rangle \right) ;$$

$$(3.59)$$

where a_0^2 is the area of the lattice's unitary cell. This gives the result

$$F = \frac{b^2}{2\pi} C_{66} \left(1 - \frac{C_{66}}{C_{11}} \right) \ln \frac{R}{a_0} , \qquad (3.60)$$

this is, the energy associated to a single dislocation depends logarithmically on the size of the crystal.

4

Melting on the colloidal crystal

4.1 The condition of melting

When isolated dislocations are present, the free energy of the crystal is affected by the increment in the internal energy –due to the work produced by the external potential that generate the dislocations– as well as by the entropy associated to these dislocations, since there are so many possible positions for a dislocation as points in the array of the crystal We will show in the next lines that this entropy contribution to the free energy determines the solid-to-liquid transition. As we pointed out in the preceding section, the elastic energy of the colloidal crystal –that we denote now as E– is given by [3]

$$E = \frac{b^2}{2\pi} C_{66} \left(1 - \frac{C_{66}}{C_{11}} \right) \ln \frac{R}{a_0} \tag{4.1}$$

There are approximately $\frac{R^2}{a_0^2}$ possible positions for a dislocation, so this is the number of accessible states for the system, having associated an elastic energy E. Then, the entropy associated to this dislocation goes as

$$S \propto \ln N = \ln \frac{R^2}{a_0^2}. \tag{4.2}$$

In this way, both the energy and the entropy of an isolated dislocation depends logarithmically on the size of the system. The free energy, considering possible variations on the temperature, $F = E - TS$, is then

$$F = \frac{b^2}{2\pi} C_{66} \left(1 - \frac{C_{66}}{C_{11}} \right) \ln \frac{R}{a_0} - 2T \ln \frac{R}{a_0}. \tag{4.3}$$

The free energy takes negative values when $T > T_m$, where

$$2T_m = \frac{b^2}{2\pi} C_{66} \left(1 - \frac{C_{66}}{C_{11}} \right). \tag{4.4}$$

When $T < T_m$, F is minimized if there is no dislocation present; if $T > T_m$, F is minimized when there are dislocations, this is, a phase transition takes place when the temperature takes a value that makes that $F = 0$, independently of the size of the system. This critical temperature at which isolated dislocations appears spontaneously will vary depending on the magnitude of the elastic moduli. The next step is to calculate the values of the shear and compression modulus, that will be determined by the nature of the interparticle potential in the lattice.

4.2   Calculus of the elastic moduli

We derive in this section the expression for the elastic moduli, in terms of the dominating interparticle potential in the lattice. If R is the vector that describe the equilibrium positions of the crystal points, and $V(\mathbf{R})$ the interaction potential between the lattice points, then the change in the free energy, due to a displacement $\mathbf{U}_n$ will be

$$F = \frac{1}{2} \sum_{n,m} [V(\mathbf{R}_n + \mathbf{U}_n - \mathbf{R}_m - \mathbf{U}_m) - V(\mathbf{R}_n - \mathbf{R}_m)], \qquad n \neq m, \qquad (4.5)$$

where both n and m enumerates the points in the crystal. The lattice points are restricted to small displacements (in agreement with our elasticity theory description), thus $\mathbf{R}$ can be expanded for $\mathbf{U}_n$ small, taking the following form:

$$F = \frac{1}{2} \sum_{n,m} \frac{1}{2} \frac{\partial U_i(r_m)}{\partial r_p} \frac{\partial U_j(r_m)}{\partial r_q} (R_n - R_m)_p (R_n - R_m)_q \frac{\partial^2 V(\mathbf{R}_n - \mathbf{R}_m)}{\partial R_i \partial R_j}. \qquad (4.6)$$

where we consider again the summation rule. Re-ordinating this expression in two independent sums, such that one of them does not depend on the potential V, we obtain

$$F = \frac{1}{4} \left(\sum_{m} \frac{\partial U_i(r_m)}{\partial r_p} \frac{\partial U_j(r_m)}{\partial r_q} \right) \left(\sum_{n} R_{np} R_{nq} \frac{\partial^2 V(\mathbf{R}_n)}{\partial R_{ni} \partial R_{nj}} \right) \qquad (4.7)$$

If $U(r_m)$ does not vary too much, we can substitute the sum over m for an integral over all the surface, this is,

$$F = \frac{n}{4} \left(\sum_{n} R_{np} R_{nq} \frac{\partial^2 V(\mathbf{R}_n)}{\partial R_{ni} \partial R_{nj}} \right) \int \frac{\partial U_i(\mathbf{r})}{\partial r_p} \frac{\partial U_j(\mathbf{r})}{\partial r_q} \, dx \, dy; \qquad (4.8)$$

here, n is the particle density, this is, $n = \frac{1}{a_0^2}$. Remembering that, at absence of dislocations, the third integral in (3.26) is zero, the energy of the crystal in terms of the elastic moduli is

$$F = \int \frac{1}{2} [C_{11}(\frac{\partial U_x}{\partial x} + \frac{\partial U_y}{\partial y})^2 + C_{66}(\frac{\partial U_x}{\partial y} - \frac{\partial U_y}{\partial x})^2 \, dx \, dy, \qquad (4.9)$$

and comparing term by term this expression with (4.8), we note that

$$C_{11} = \frac{n}{2}\sum_n R_{nx}^2 \frac{\partial^2 V(\mathbf{R}_n)}{\partial R_{nx}^2} ; \tag{4.10}$$

$$C_{66} = \frac{n}{2}\sum_n R_{ny}^2 \frac{\partial^2 V(\mathbf{R}_n)}{\partial R_{nx}^2} . \tag{4.11}$$

If V depends only on the magnitude of $\mathbf{R}_n$, as in our case, this can be written as

$$C_{11} = \frac{n}{2}\sum_n [n_x^4 R_n^2 V''(R_n) + (n_x^2 - n_x^4) R_n V'(R_n)] \tag{4.12}$$

and

$$C_{66} = \frac{n}{2}\sum_n [n_x^2 n_y^2 R_n^2 V''(R_n) + n_y^2(1 - n_x^2) R_n V'(R_n)] , \tag{4.13}$$

where $n_i = \frac{R_{ni}}{R_n}$. Instead of this, we can use the averaged values

$$\langle n_x^2 \rangle = \tfrac{1}{2}, \qquad \langle n_x^4 \rangle = \tfrac{3}{8}, \qquad \langle n_x^2 n_y^2 \rangle = \tfrac{1}{8}, \tag{4.14}$$

and obtain

$$C_{11} = \frac{n}{16}\sum_n [3R_n^2 V''(R_n) + R_n V'(R_n)] , \tag{4.15}$$
$$C_{66} = \frac{n}{16}\sum_n [R_n^2 V''(R_n) + 3R_n V'(R_n)] .$$

Now we have explicit expressions for the elastic moduli, in terms of the interparticle potential. In the following section we will consider the case of magnetic interactions between points of the colloidal crystal and use these expressions to find the condition of melting of the system.

4.3 Colloids in a magnetic field

In this section we consider the specific case of colloidal particles in a magnetic field. Each particle acquires a magnetic moment μ proportional to the magnetic induction B. If this induction is high enough, the interaction energy $V(R_n)$ is dominated by the magnetic dipole interaction

$$V(R_n) = \frac{\mu^2}{R_n^3} , \tag{4.16}$$

where R_n is the from the n-th point to the origin. Then the elastic moduli reduces to

$$C_{11} = \frac{33\mu^2 n}{16} \sum_n \frac{1}{R_n^3}, \qquad\qquad C_{66} = \frac{3\mu^2 n}{16} \sum_n \frac{1}{R_n^3}, \qquad n \neq 0, \qquad (4.17)$$

that is to say $C_{11} = 11 C_{66}$. The sum can be calculated in the following form. The lattice points can be arranged in such a way that

$$R_x = nb + m\frac{b}{2}, \qquad\qquad R_y = m\frac{b\sqrt{3}}{2}, \qquad (4.18)$$
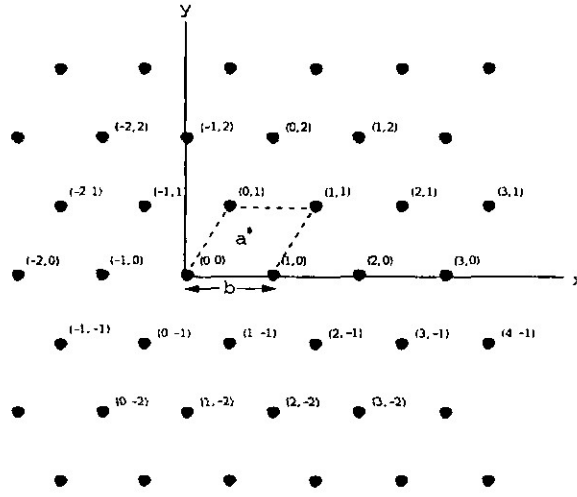
as indicated in the figure 4.1.

Figure 4.1: Hexagonal two-dimensional lattice, arranged in pairs (n, m). a_0^2 is the area of the unitary cell, and b is the lattice parameter.

The sum over $\frac{1}{R_n^3}$ reduces to

$$\sum_n \frac{1}{R_n^3} = \frac{2^3}{b^3} \sum_{n,m} \frac{1}{[3m^2 + (2n + m)^2]^{\frac{3}{2}}}, \qquad (4.19)$$

with $\{n, m\} \neq \{0, 0\}$. The sum of the right can be estimated, and it gives a value of 1.373638. As can be seen from the figure, $b = (\frac{2}{\sqrt{3}n})^{\frac{1}{2}}$ and then, in terms of the density n, the elastic moduli C_{66} gives

$$C_{66} = \frac{3^{\frac{7}{4}}}{4\sqrt{2}} \mu^2 n^{\frac{5}{2}} \sum_{n,m} \frac{1}{[3m^2 + (2n + m)^2]^{\frac{3}{2}}}, \qquad \{n, m\} \neq \{0, 0\}. \qquad (4.20)$$

With this result, we can write the melting condition (4.4) as

$$A\frac{b^2}{2\pi}C_{66}(1 - \frac{C_{66}}{C_{11}}) - 2T = 0.$$ (4.21)

The factor A is due to the effect of screening of dislocation pairs [9]. In terms of the moment μ and the density n, an equivalent relation reads

$$\frac{T_m}{\mu^2 n^{\frac{3}{2}}} = \frac{15 \cdot 3^{\frac{1}{4}}}{44\sqrt{2\pi}}A \sum_{n,m} \frac{1}{[3m^2 + (2n+m)^2]^{\frac{3}{2}}}. \qquad \{n,m\} \neq \{0,0\}.$$ (4.22)

After the numerical calculation of this sum, one can write down the final formula, for the solid-liquid boundary, as

$$\frac{T_m}{\mu^2 n^{\frac{3}{2}}} = 0.1387A.$$ (4.23)

The theoretical estimate gives $A = 0.65$ [9].

5

Conclusions

The phase diagram (4.23) of the colloidal system is the main issue of this work. The melting condition depends only on temperature, two-dimensional particle density, and the magnetic moment, which is linearly proportional to the magnetic field. The experimental data [6] confirm the phase diagram of the type (4.23). The numerical value in the right-hand side of equation (4.23) is to be compared with more accurate experimental results to be provided in the nearest future.

Let us summarize the results:

1. expressions for elastic modulus for a colloidal system in a magnetic field are derived;

2. the melting condition of a colloidal crystal in a magnetic field is obtained;

3. the magnetic field, at which the phase transition occurs, $B_m \sim T^{\frac{1}{2}} n^{-\frac{3}{4}}$ is schematically plotted in figure 5.1. The experimental measurement of such melting curve gives the same functional dependence in terms of B_m and n [6]. The experimental verification of the numerical value in the right-hand side of (4.23) is in progress [6].
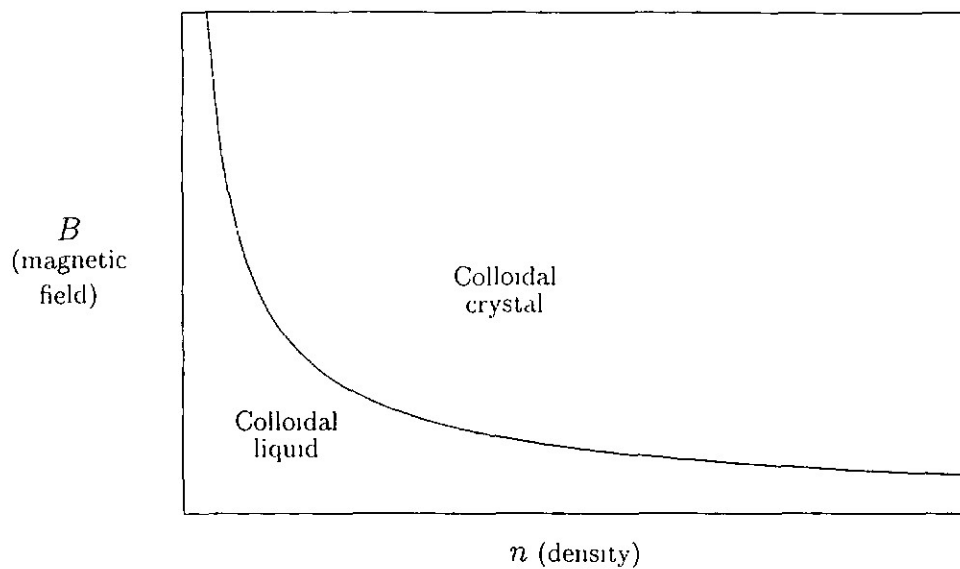
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Figure 5.1: Schematic phase diagram of the colloidal system in the magnetic field $(B_m \sim T^{\frac{1}{2}} n^{-\frac{3}{4}})$, where n is the concentration of colloidal particles.

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