TD2 : Nematic liquid crystals

Statistical Mechanics – iCFP M2

Liquid crystal are small rod-like molecules whose optical properties are used, *e.g.*, in your laptop display. They acquire some of these properties by undergoing a first-order phase transition toward long-range orientational order upon an increase of their density. This so-called isotropic to nematic transition is the prototype of the emergence of order in soft matter systems, and studying it is the occasion for us to train in several powerful statistical mechanical techniques.

In Sec. 1, we derive an approximate form for the orientational free energy of a homogeneous liquid crystal solution using a variational ansatz. Sec. 2 then uses a double tangent construction to study phase coexistence based on this free energy. In Sec. 3 we turn to inhomogeneous solutions, and derive the corresponding free energy functional using Landau theory.

This problem sheet was inspired by Refs. [1, 2].

1 Orientational free energy/variational ansatz

Consider a homogeneous solution of liquid crystals. Would the little rods rather align together (as favored by their translational entropy) or point in random directions (as favored by their rotational entropy)? This can in principle only be answered by solving for the rods' preferred orientational distribution, a very difficult problem.

Here we tread in Onsager's footsteps and approximate the space of these distributions by a one-parameter family of distributions, which already give good results. Establishing this type of upper bounds on the free energy of a complicated system through a well-chosen ansatz is the basis of the widely used density functional theories (DFT).

1.1 Quasi-ideal solution

We consider a dilute solution of molecules of concentration c dispersed in a solvent. The free energy per unit volume reads

$$f = kT\left[c\ln\frac{c}{c_0} + A_2\,c^2\right], \tag{1}$$

where A_2 is the second virial coefficient and c_0 some (irrelevant) reference fixed concentration. Internal degrees of freedom are discarded.

1.1.1 Read the first appendix, taken from Ref. [3]. Express the virial coefficient as a function of the interaction potential between the molecules. What are its units? Discuss its relationship to the excluded volume, and why it is representative of two-body interactions. In what limit is Eq. (1) valid?

1.1.2 What is its value for hard spheres of radius a ?

1.1.3 Defining $F = Vf$, the osmotic pressure is defined as

$$\Pi = -\left.\frac{\partial F}{\partial V}\right|_{N,T}, \tag{2}$$

i.e., as the change in free energy upon a change in the system's volume V while leaving the number N of liquid crystal molecules constant. Show that $\Pi = c\mu - f$ in general [*i.e.*, whether or not Eq. (1) is valid], where μ is for the chemical potential of the liquid crystal molecules.

1.2 Virial coefficient between rods

We now consider very anisotropic rod-like molecules whose length L is much larger than their radius a. At variance with the previous discussion, molecule are now endowed with an internal degree of freedom: their orientation.

1.2.1 We start with a qualitative discussion of the isotropic to nematic transition. You may find inspiration in the first page of the appended paper entitled "Order through entropy" [4] (reading the rest of the paper is forbidden). Under what concentration regime do you expect the rods to align? Why does this happen? What is the only dimensionless parameter controlling the phase behavior of the system? Reconstruct the associated critical concentration from a simple scaling argument.

1.2.2 Show that two rods separated by a fixed angle γ interacting sterically have a virial coefficient $A_2 = Ab(\gamma)$, where $A = aL^2$ and $b(\gamma) = 2|\sin\gamma|$.

1.3 Thermodynamics of a solution of rods

In a solution of rods, the molecules adopt all possible orientations. We will identify the orientation of a rod by the unitary vector $\hat{\mathbf{n}}$ and we will denote by $c(\hat{\mathbf{n}}) = c\Psi(\hat{\mathbf{n}})$ the concentration of rods with orientation $\hat{\mathbf{n}}$ (in other words Ψ is the probability distribution function for the rods' orientations). We are working here under conditions where c is fixed.

1.3.1 Remembering the meaning of A_2 as related to two-body interactions, what is the free energy of the solution as a function of c and Ψ?

1.3.2 Determine the rods' chemical potential and the osmotic pressure. We will denote $\mu_0 = \int \Psi(\hat{\mathbf{n}}) \log \Psi(\hat{\mathbf{n}})\, \mathrm{d}\hat{\mathbf{n}}$ and $b_0 = \int \Psi(\hat{\mathbf{n}})\Psi(\hat{\mathbf{n}}')b(\hat{\mathbf{n}}, \hat{\mathbf{n}}')\, \mathrm{d}\hat{\mathbf{n}}\, \mathrm{d}\hat{\mathbf{n}}'$.

1.4 Orientational distribution

1.4.1 What physical rule should be applied to find the orientational distribution $\Psi(\hat{\mathbf{n}})$?

1.4.2 Write the integral equation satisfied by the probability distribution Ψ, not forgetting to introduce a Lagrange multiplier to ensure its normalization (see appendix for a reminder about Lagrange multipliers).

1.4.3 Show that this equation always has a trivial isotropic solution.

1.4.4 For high enough concentrations, the integral equation also has another solution. To avoid a full computation, Onsager proposed a variational method based on the family of functions

$$\Psi(\hat{\mathbf{n}}) \propto \cosh(\alpha \cos\theta), \tag{3}$$

where θ is the colatitude of the usual spherical coordinates assuming the overall direction of alignment of the nematic is z. What is the qualitative meaning of the parameter α? Normalize this distribution.

1.4.5 Express the free energy as a function of the single parameter α. You need not compute the not-so-appetizing integrals involved.

1.4.6 The free energy as a function of α is given in Fig. 1(a). What is the α chosen by the system?

1.4.7 Having chosen α, and assuming the system is in a pure phase, how would you determine whether the isotropic or the nematic phase is most stable?

1.4.8 The nematic order parameter is defined as

$$S = \left\langle \frac{3\cos^2\theta - 1}{2} \right\rangle. \tag{4}$$

Explain this choice. What is its value in the isotropic phase? What is its value in the nematic phase (as a function of α)?

Note that as most order parameters, S can be seen as a first order derivative of the free energy with respect to some external field. This is apparent in your homework assignment, where $\langle \cos^2\theta \rangle$ is clearly proportional to the derivative of F with respect to the magnetic field H.

1.4.9 Qualitatively draw the phase diagram (*e.g.*, the diagram specifying what phase is expected as a function of the relevant physical parameters) of the isotropic-to-nematic phase transition for a monophasic system. We denote the critical concentration by c_c.

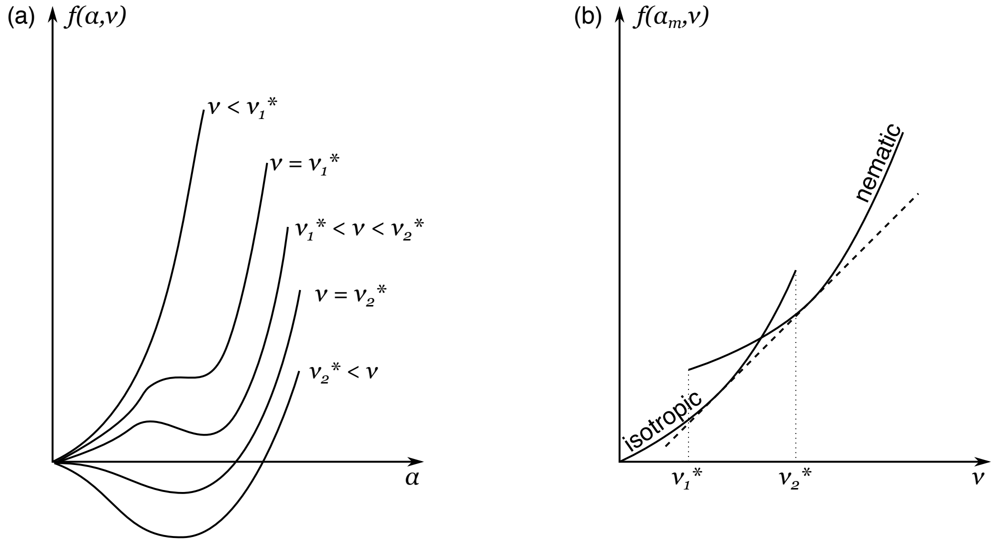

Figure 1: Free energy profile as a function of α and the dimensionless parameter $\nu = caL^2$. (a) Meaning of ν_1^* and ν_2^* (b) Free energy per unit volume corresponding to the two minima α_m of $f(\alpha, \nu)$ with respect to α as a function of ν, corresponding to the isotropic and nematic phases respectively. After Ref. [1].

2 Isotropic-nematic transition/theory of first-order transitions

Knowing that the liquid crystal can exist in two phases, we now ask whether these phases can coexist and under what conditions. We thus use the bitangent construction, a very useful tool to study first order transitions.

2.1 Elementary thermodynamic considerations

2.1.1 What are the two equilibrium conditions between an isotropic phase and a nematic phase? Write these conditions formally.

2.1.2 Using the results of Sec. 1, show through dimensional analysis that the concentrations in each phase are proportional to $1/aL^2$.

2.1.3 Using Fig. 1(a), discuss the order of the transition.

2.1.4 Assuming the system stays within a single phase, how can you read out its free energy as a function of $\nu = caL^2$ on Fig. 1(b)?

2.2 Landau free energy

Rather than dealing with the complicated form of $f(\alpha, \nu)$ derived from Sec. 1, a convenient approach is to express the free energy density as a generic function of the order parameter S defined in Eq. (4). This approach assumes that S remains small enough that $f(S, \nu)$ can be Taylor-expanded close to $S = 0$, and here we use it to rationalize the shape of the curves presented in Fig. 1.

2.2.1 Assuming that $\mathfrak{f}(S, \nu) = f(S, \nu) - f(0, \nu)$ has to have a minimum at $S = 0$ consistent with the existence of an isotopic phase, to what order in S do you have to expand $\mathfrak{f}$ to obtain the same type of secondary minimum for $S > 0$ that we observe in Fig. 1(a)?

2.2.2 The appearance of the minimum is controlled by the dimensionless concentration ν. To represent this qualitative behavior, express one of the coefficients of your expansion as a linear function of ν. In this simplified approach we assume that the other coefficients are constant with ν.

2.2.3 Rescale and shift $\mathfrak{f}$, S and ν to find

$$\tilde{\mathfrak{f}}(\tilde{S}, \tilde{\nu}) = (1 - \tilde{\nu})\tilde{S}^2/2 - 2\tilde{S}^3/3 + \tilde{S}^4/4, \tag{5}$$

where tildes denote rescaled and/or shifted versions of the original variables. At what concentration $\tilde{\nu}_1^*$ does the secondary minimum of Fig. 1(a) appear? At what concentration $\tilde{\nu}_c$ does it become more stable than the isotropic solution? In this model, what is the concentration $\tilde{\nu}_2^*$ introduced in Fig. 1(b)?

In the following we drop tildes to lighten the notation.

2.3 Phase coexistence

For a certain range of average concentration ν it is energetically more favorable for a system of fixed volume V to separate into two phases of different densities ν_A and ν_B. Here we determine these conditions and the nature of these two phases by a general geometrical method known as the bitangent construction. In the following we keep our discussion general and do not explicitly refer to the specific form of Eq. (5).

2.3.1 Show that due to the conservation of volume and of the number of liquid crystal molecules

$$f = f_A + \frac{\nu - \nu_A}{\nu_B - \nu_A}(f_B - f_A), \tag{6}$$

where f, f_A and f_B are the average free energy per unit volume of the diphasic system, of the pure phase A and of the pure phase B, respectively. Deduce from this a geometric construction involving drawing a line between two points A and B belonging to the isotropic and nematic curve respectively to read on the curve of Fig. 1(b) the free energy of the diphasic system.

2.3.2 How should you choose ν_A and ν_B for the free energy of the system to be minimal? We will denote this choice by (ν_A^*, ν_B^*).

2.3.3 What thermodynamic quantity does the slope of the bitangent involved in this construction correspond to? How about its vertical intercept? Using these observations show that the geometrical construction discussed above is equivalent to the balance of both osmotic pressure and chemical potential between the two phases.

2.3.4 Plot the phase diagram of the liquid crystal as a function of ν, indicating the positions of ν_1^*, ν_2^*, ν_A^*, ν_B^* and the critical concentration ν_c associated with the phase diagram of Sec. 1 with respect to the region of coexistence.

Bonus question

The state equation of the Van der Waals fluid is given by (up to a term independent on V):

$$F = -\frac{N}{\beta}\ln\left(\frac{V}{N} - \frac{v}{2}\right) - \frac{N^2 A}{V}, \tag{7}$$

where A is a constant and v is the excluded volume associated with a particle of the fluid. From the principles of the bitangent construction, determine the critical temperature and pressure of the fluid's liquid-gas phase transition. Reconstruct its full (P, V) phase diagram (binodal and spinodal).

3 Deformation free energy/construction of a Landau functional

We now consider a liquid crystal deep in the nematic phase, implying that its nematic order parameter has a fixed, almost constant value. While the corresponding magnitude of the local rod orientation does not vary, its alignment direction can. To estimate the cost of such deformations, we move away from the microscopic description developed in Sec. 1, and attempt to infer a minimal form of the liquid crystal free energy guided only by symmetry considerations. This is the general strategy used in constructing a Landau theory.

The local orientation of the rods is described by the nematic director field $\hat{\mathbf{n}}(\mathbf{r})$, where $\hat{\mathbf{n}}$ is a unit vector and $\mathbf{r}$ denotes the vector of spatial coordinates, which we will restrict to two dimensions for simplicity. Assuming that our rods are up-down symmetric, the system must be invariant under the transformation $\hat{\mathbf{n}} \to -\hat{\mathbf{n}}$. In two dimensions, we can equivalently parametrize our alignment field by the angle $\phi(\mathbf{r})$ between $\hat{\mathbf{n}}$ and the horizontal axis. Considering slow spatial variations, we write the free energy functional of the system as a Taylor expansion in powers of the gradient:

$$F = \int \left[\alpha(\phi) + \beta_i(\phi)(\nabla_i\phi) + \gamma_{ij}(\phi)(\nabla_i\phi)(\nabla_j\phi) + \mathcal{O}(\nabla^3)\right] \mathrm{d}x\mathrm{d}y, \tag{8}$$

were the Einstein summation rule is used and where $\alpha(\phi)$, $\beta_i(\phi)$ and $\gamma_{ij}(\phi)$ are *a priori* unknown functions whose form we set out to determine from the symmetries of the system.

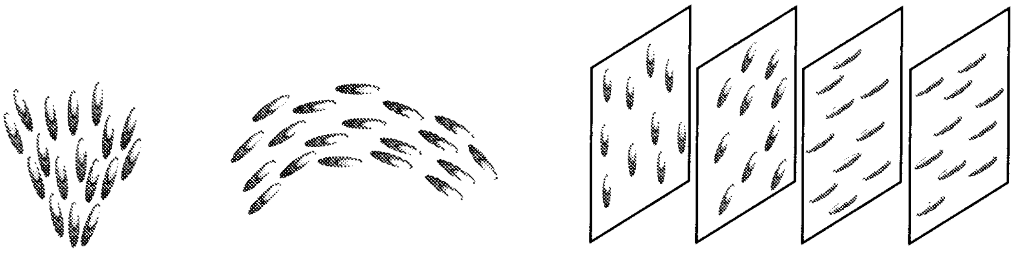
(a) (b) (c)

Figure 2: The three independent types of deformation for the nematic order parameter, know as splay (a), bend (b) and twist (c). Adapted from Ref. [2].

3.1 Preliminaries

3.1.1 Why are we justified in keeping only the lowest terms of the gradient expansion?

3.1.2 Considering only the zeroth order term (*e.g.*, in a situation where ϕ is the same everywhere), we consider a solid rotation of the system, *i.e.*, a simultaneous rotation of $\mathbf{n}$ and $\mathbf{r}$ by an angle ϕ_0 (or equivalently a rotation of the coordinate axes leaving the system untouched). How are the new variables ϕ', x', y' related to the old ones (ϕ, x, y)?

3.1.3 The free energy of the system should be invariant under such a transformation. Why is that? To order 0, how is the free energy of Eq. (8) transformed under this rotation?

3.1.4 Conclude from this that α is a constant and can thus be dropped.

3.1.5 Now consider the first order term. How should the free energy transform under the reflection symmetry $\mathbf{r} \to -\mathbf{r}$ (or equivalently a rotation of the system axes by π followed by an inversion of the polarity of each individual molecule)? Deduce from this the form of $\beta_i(\phi)$.

3.2 Second order terms

3.2.1 Equation (8) does not include second order terms of the form $\tilde{\gamma}(\phi)\nabla_i\nabla_j\phi$. Show through an integration by part that this does not restrict its generality.

3.2.2 We again consider the same rotation as in question 3.1.2. How are the new differential operators ∇'_i related to the old? What constraints does the invariance of the free energy put on the functions γ_{ij}?

3.2.3 Using an infinitesimal rotation $\phi_0 \ll 1$, show that these conditions yield the system of equations:

$$\partial_\phi\gamma_{11} = -\gamma_{12} - \gamma_{21} \tag{9a}$$
$$\partial_\phi\gamma_{12} = \gamma_{11} - \gamma_{22} \tag{9b}$$
$$\partial_\phi\gamma_{21} = \gamma_{11} - \gamma_{22} \tag{9c}$$
$$\partial_\phi\gamma_{22} = \gamma_{12} + \gamma_{21} \tag{9d}$$

3.2.4 Solve Eqs. (9) to show that F takes the following form:

$$F = \int \{ C\,(\nabla\phi)^2 + (A\cos 2\phi + B\sin 2\phi)\ \left[(\nabla_x\phi)^2 - (\nabla_y\phi)^2\right] + (2A\sin 2\phi - 2B\cos 2\phi)\,(\nabla_x\phi)\,(\nabla_y\phi)\,\}\,\mathrm{d}x\mathrm{d}y, \tag{10}$$

where A, B and C are undetermined constants.

3.2.5 Use reflection symmetry to kill a few more terms.

3.2.6 Show that the resulting free energy can be rewritten in terms of the two quantities $\nabla\cdot\hat{\mathbf{n}}$ and $\hat{\mathbf{n}}\times(\nabla\times\hat{\mathbf{n}})$ only.

3.2.7 This free energy is known as the Frank free energy. Its more general, three-dimensional form is

$$F = \int \left\{ \frac{K_1}{2}(\nabla \cdot \hat{\mathbf{n}})^2 + \frac{K_2}{2}[\hat{\mathbf{n}} \cdot (\nabla \times \hat{\mathbf{n}})]^2 + \frac{K_3}{2}[\hat{\mathbf{n}} \times (\nabla \times \hat{\mathbf{n}})]^2 \right\} \mathrm{d}\mathbf{r}. \tag{11}$$

The constants K_1, K_2 and K_3 are associated with the three types of deformation illustrated in Fig. 2. Which is which? Why is one of these terms missing in 2D? What is their sign? For PAA at 120°C $K_1 = 7\,\mathrm{pN}$, $K_2 = 4.3\,\mathrm{pN}$ and $K_3 = 17\,\mathrm{pN}$ [5]. Can you rationalize this order of magnitude from dimensional analysis?

3.2.8 Why could we assume that the magnitude of the nematic order parameter was fixed in this analysis?

4 What's next?

The Frank free energy derived above is widely used as the basis for many studies of liquid crystals where the spatial structure of the nematic field plays a role. One such example is the discussion of the turbidity of nematics included in your homework assignment. Another one, the Fréedericksz transition, forms the basis of liquid crystal displays and will be studied by students of the Soft Matter and Biophysics in their Soft Matter course. Anticipating on the next tutorial, we can also note that in two dimensions the case $K_1 = K_3$ gives $F \propto \int (\nabla\phi)^2$, which is the energy functional of the XY model. This illustrates the broad relevance of the symmetry considerations developed here.

References

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[4] Daan Frenkel. Order through entropy. *Nat. Mater.*, 14:9–12, 2015.

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CHAPTER VII

NON-IDEAL GASES

§ 74. Deviations of gases from the ideal state

THE equation of state of an ideal gas can often be applied to actual gases with sufficient accuracy. This approximation may, however, be inadequate, and it is then necessary to take account of the deviations of an actual gas from the ideal state which result from the interaction between its component molecules.

Here we shall do this on the assumption that the gas is still so rarefied that triple, quadruple, etc., collisions between molecules may be neglected, and their interaction may be assumed to occur only through binary collisions.

To simplify the formulae, let us first consider a monatomic actual gas. The motion of its particles may be treated classically, so that its energy has the form

$$E(p, q) = \sum_{a=1}^{N} \frac{p_a^2}{2m} + U, \tag{74.1}$$

where the first term is the kinetic energy of the N atoms of the gas, and U is the energy of their mutual interaction. In a monatomic gas, U is a function only of the distances between the atoms. The partition function $\int e^{-E(p,q)/T}\,d\Gamma$ becomes the product of the integral over the momenta of the atoms and the integral over their coordinates. The latter integral is

$$\int \ldots \int e^{-U/T}\,dV_1 \ldots dV_N,$$

where the integration over each $dV_a = dx_a\,dy_a\,dz_a$ is taken over the whole volume V occupied by the gas. For an ideal gas, $U = 0$, and this integral would be simply V^N. It is therefore clear that, on calculating the free energy from the general formula (31.5), we obtain

$$F = F_{\text{id}} - T \log \frac{1}{V^N} \int \ldots \int e^{-U/T}\,dV_1 \ldots dV_N, \tag{74.2}$$

where F_{id} is the free energy of an ideal gas.

Adding and subtracting unity in the integrand, we can rewrite formula (74.2) as

$$F = F_{\text{id}} - T \log \left\{ \frac{1}{V^N} \int \ldots \int (e^{-U/T} - 1)\,dV_1 \ldots dV_N + 1 \right\}. \tag{74.3}$$

For the subsequent calculations we make use of the following formal device. Let us suppose that the gas is not only sufficiently rarefied but also so small in quantity that not more than one pair of atoms may be assumed to be colliding in the gas at any one time. This assumption does not affect the generality of the resulting formulae, since we know from the additivity of the free energy that it must have the form $F = Nf(T, V/N)$ (see § 24), and therefore the formulae deduced for a small quantity of gas are necessarily valid for any quantity.

The interaction between atoms is very small except when the two atoms concerned are very close together, i.e. are almost colliding. The integrand in (74.3) is therefore appreciably different from zero only when some pair of atoms are very close together. According to the above assumption, not more than one pair of atoms can satisfy this condition at any one time, and this pair can be selected from N atoms in $\frac{1}{2}N(N-1)$ ways. Consequently, the integral in (74.3) may be written

$$\tfrac{1}{2}N(N-1) \int \ldots \int (e^{-U_{12}/T} - 1)\,dV_1 \ldots dV_N,$$

where U_{12} is the energy of interaction of the two atoms (it does not matter which two, as they are all identical); U_{12} depends only on the coordinates of two atoms, and we can therefore integrate over the remaining coordinates, obtaining V^{N-2}. We can also, of course, write N^2 instead of $N(N-1)$, since N is very large; substituting the resulting expression (74.3) in place of the integral, and using the fact that $\log(1+x) \cong x$ for $x \ll 1$, we have†

$$F = F_{\text{id}} - \frac{TN^2}{2V^2} \iint (e^{-U_{12}/T} - 1)\,dV_1\,dV_2,$$

where $dV_1\,dV_2$ is the product of differentials of the coordinates of the two atoms.

But U_{12} is a function only of the distance between the two atoms, i.e. of the differences of their coordinates. Thus, if the coordinates of the two atoms are expressed in terms of the coordinates of their centre of mass and their relative coordinates, U_{12} will depend only on the latter (the product of

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† We shall see later that the first term in the argument of the logarithm in (74.3) is proportional to N^2/V. The expansion in question therefore depends on precisely the assumption made above, that not only the density N/V but also the quantity of the gas is small.

whose differentials will be denoted by dV). We can therefore integrate with respect to the coordinates of the centre of mass, again obtaining the volume V. The final result is

$$F = F_{id} + N^2TB(T)/V, \tag{74.4}$$

where

$$B(T) = \tfrac{1}{2}\int (1 - e^{-U_{12}/T})\, dV. \tag{74.5}$$

From this we find the pressure $P = -\partial F/\partial V$:

$$P = \frac{NT}{V}\left(1 + \frac{NB(T)}{V}\right), \tag{74.6}$$

since $P_{id} = NT/V$. Equation (74.6) is the equation of state of the gas in the approximation considered.

As we know from the theorem of small increments (§ 15), the changes in the free energy and the thermodynamic potential resulting from small changes in the external conditions or properties of a body are equal, one being taken at constant volume and the other at constant pressure.

If we regard the deviation of a gas from the ideal state as such a change, we can change directly to Φ from (74.4). To do so, we need only express the volume in terms of the pressure in the correction term in (74.4) by means of the equation of state for an ideal gas, obtaining

$$\Phi = \Phi_{id} + NBP. \tag{74.7}$$

The volume may hence be expressed as a function of the pressure:

$$V = \frac{NT}{P} + NB. \tag{74.8}$$

The whole of the foregoing discussion applies to monatomic gases. The same formulae remain valid, however, for polyatomic gases also. In this case the potential energy of interaction of the molecules depends not only on their distance apart but also on their relative orientation. If (as almost always happens) the rotation of the molecules may be treated classically, we can say that U_{12} is a function of the coordinates of the centres of mass of the molecules and of rotational coordinates (angles) which define the spatial orientation of the molecules. It is easy to see that the only difference from the case of a monatomic gas amounts to the fact that dV_a must be taken as the product of the differentials of all these coordinates of the molecule. But the rotational coordinates can always be so chosen that the integral $\int dV_a$ is again equal to the volume V of the gas. For the integration over the coordinates of the centre of mass gives this volume V, while the integration over angles gives a constant, and the angles can always be normalised so that this constant is unity. Thus all the formulae derived in this section have the

same form for polyatomic gases, the only difference being that in (74.5) dV is now the product of the differentials of coordinates defining both the distance between two molecules and their relative orientation.[†]

All the above formulae are meaningful, of course, only if the integral (74.5) converges. For this to be so it is certainly necessary that the forces of interaction between the molecules should decrease sufficiently rapidly with increasing distance: U_{12} must decrease at large distances more rapidly than $1/r^3$.[‡]

If this condition is not satisfied, a gas consisting of identical particles cannot exist as a homogeneous body. In this case every region of matter will be subject to very large forces exerted by distant parts of the gas. The regions near to and far from the boundary of the volume occupied by the gas will therefore be in quite different conditions, and so the gas is no longer homogeneous.

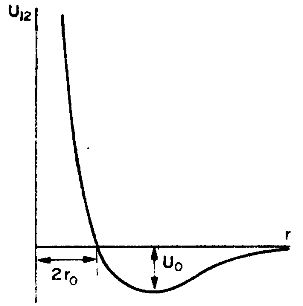

FIG. 11

For monatomic gases the function $U_{12}(r)$ has the form shown in Fig. 11; the abscissa is the distance r between the atoms. At small distances, U_{12} increases with decreasing distance, corresponding to repulsive forces between the atoms; beginning approximately at the place where the curve crosses the abscissa axis, it rises steeply, so that U_{12} rapidly becomes very large, corresponding to the mutual "impenetrability" of the atoms (for which reason the distance r_0 is sometimes called the radius of the atom). At large distances, U_{12} increases slowly, approaching zero asymptotically. The increase of U_{12} with distance corresponds to a mutual attraction of the atoms. The minimum

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[†] If the particles in the gas have spin, the form of the function U_{12} depends in general on the orientation of the spins. In that case a summation over spin orientations must be added to the integration with respect to dV.

[‡] This condition is always satisfied for atomic and molecular gases: the forces of interaction between electrically neutral atoms or molecules (including dipoles), when averaged over the relative orientations of the particles, decrease at large distances as $U_{12} \propto 1/r^6$; see *Quantum Mechanics*, § 89.

of U_{12} corresponds to a stable equilibrium. The absolute value U_0 of the energy at this point is usually small, being of the order of the critical temperature of the substance.

For a polyatomic gas, the interaction energy has a similar form, but it cannot, of course, be represented by the curve in Fig. 11, since it is a function of a larger number of variables.

This information as to the nature of the function U_{12} is sufficient to determine the sign of $B(T)$ in the limiting cases of high and low temperatures. At high temperatures ($T \gg U_0$) we have $|U_{12}|/T \ll 1$ throughout the region $r > 2r_0$, and the integrand in $B(T)$ (74.5) is almost zero. Thus the value of the integral is mainly determined by the region $r < 2r_0$, where U_{12}/T is large and positive; in this region, therefore, the integrand is positive, and so the integral itself is positive. Thus $B(T)$ is positive at high temperatures.

At low temperatures ($T \ll U_0$), on the other hand, the region $r > 2r_0$ is the important one in the integral, and in this region U_{12}/T is large and negative. At sufficiently low temperatures, therefore, $B(T)$ must be negative, and its temperature dependence is essentially given by the exponential factor $-e^{U_0/T}$.

Being positive at high temperatures and negative at low temperatures, $B(T)$ must pass through zero at some temperature.[†]

Finally, let us consider a Joule–Thomson process involving a non-ideal gas. The variation of temperature during the process is given by the derivative

$$\left(\frac{\partial T}{\partial P}\right)_W = \frac{1}{C_p}\left[T\left(\frac{\partial V}{\partial T}\right)_P - V\right]; \qquad (74.9)$$

see (18.2). For an ideal gas this derivative is of course zero, but for a gas with the equation of state (74.8) we have

$$\left(\frac{\partial T}{\partial P}\right)_W = \frac{N}{C_p}\left(T\frac{\mathrm{d}B}{\mathrm{d}T} - B\right) = \frac{N}{2C_p}\int\left[e^{-U_{12}/T}\left(1 - \frac{U_{12}}{T}\right) - 1\right]\mathrm{d}V. \qquad (74.10)$$

As in the discussion of $B(T)$, it is easy to see that at high temperatures $(\partial T/\partial P)_W < 0$, i.e. when the gas goes from a higher to a lower pressure in a Joule–Thomson process its temperature rises; at low temperatures, $(\partial T/\partial P)_W > 0$, i.e. the gas temperature falls with the pressure. At a definite temperature for each gas, called the ***inversion point***, the Joule–Thomson effect must therefore change sign.[‡]

[†] The temperature T_B for which $B(T_B) = 0$ is called the *Boyle point*. If PV/T is plotted against P for various given T, the isotherm $T = T_B$ has a horizontal tangent as $P \to 0$, and separates isotherms with positive and negative initial slopes; all the isotherms start from the point $PV/T = 1$, $P = 0$.

[‡] It will be recalled that we are considering a gas which is only slightly non-ideal, so that the pressure is relatively low. The result that the inversion point is independent of pressure is valid only in this approximation; cf. § 76, Problem 4.

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Order through entropy

Daan Frenkel

Understanding entropic contributions to common ordering transitions is essential for the design of self-assembling systems with addressable complexity.

Irreversible changes in physical systems — such as the breaking of a glass on hitting the floor or the formation of a crystal from its melt — only occur because of an increase in entropy (Box 1). Yet the formation of a crystal seems to be at odds with the widespread notion of entropy as a measure of disorder. If, under the same conditions, a crystal does indeed have lower entropy than the melt from which it forms, does this mean that crystallization cannot happen? The answer is, of course, that crystallization can occur because the system is in contact with the environment: on freezing, the heat released increases the entropy of the surroundings by an amount that is larger than the entropy decrease incurred in the transition from liquid to crystal.

However, the situation becomes more interesting when considering systems that cannot release heat to 'pay' for a local decrease in entropy. Hard (colloidal) particles — that is, particles that cannot overlap with each other and for which the internal energy does not depend on particle arrangement — are an example. Can such athermal systems order spontaneously? This would only be possible if the entropy of the ordered phase were higher than that of the disordered phase at the same density and temperature. Clearly, such an ordering transition would not be possible if entropy were a measure of visible disorder. However, over the past decades many examples have emerged where athermal systems do undergo transitions that increase both visible order and entropy.

Entropic ordering

To my knowledge, the earliest example of a system that has an ordered phase with higher entropy than that of the disordered phase at the same density is Lars Onsager's model for a fluid of

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Box 1 | A brief explanation of entropy.

Just as in biology 'nothing makes sense except in the light of evolution'[18], the spontaneous changes that take place in macroscopic physicochemical systems cannot be understood except in the light of the second law of thermodynamics. The second law emerged from the simple, empirical observation that heat does not spontaneously flow from a cooler to a hotter body. Rudolf Clausius showed that this observation implies that there is a quantity — which he called entropy and defined in a sentence spanning 14 lines — that always increases during irreversible changes in isolated systems[19]. In the final sentence of his 1865 paper, Clausius summarized the implications of his momentous finding by stating that the entropy of the Universe tends to a maximum. Few laws in physics seem to be based on stronger evidence than the second law.

Clausius gave no microscopic interpretation of entropy. It was instead Ludwig Boltzmann, Willard Gibbs and Max Planck who established the relation between entropy and the atomistic description of nature. This relation is captured by the equation $S = k_B \ln W$, which is chiselled into Boltzmann's gravestone (even though Boltzmann never wrote 'his' equation in this form; Planck was the first to do so[20,21]). The equation states that the entropy, S, is equal to the logarithm of the number of states accessible to the system, W, multiplied by a constant (Boltzmann's constant, k_B).

The second law then implies that an irreversible change in a closed system is only possible if the number of states that correspond to the final state is (much) larger than that of the initial state. In classical statistical mechanics, the 'number of states' gets replaced by the accessible volume in phase-space, but the basic statement of the second law remains the same: systems do not move spontaneously from a large volume in phase space to a (much) smaller one. The word 'much', however, requires a comment. When the entropy of a system is increased by only one joule per kelvin (a change of less than 0.1% for one litre of ambient water), then the number of accessible states increases by the staggering factor $10^{10^{22.5}}$, a number so large that it cannot be captured by any analogy that makes sense.

thin, hard rods[1]. Onsager's work returns time and again when considering phase transitions where ordering is associated with an increase in entropy: in every case, there are several contributions to the entropy — in Onsager's case, the entropy associated with the translational and orientational degrees of freedom of the rods — and ordering takes place because at the transition one contribution is larger than the other.

In fact, Onsager's theory describes the transition from an isotropic (orientationally disordered) fluid phase to a nematic (orientationally ordered) phase of thin, hard rods. In the nematic phase, the rods are, on average, aligned parallel to each other, but not perfectly so: there is a spread in their orientations around the average alignment direction. To understand orientational entropy, one can assume that the number of possible orientations of the rods is a large but finite number, M. Then a fluid of hard rods can be viewed as a mixture of M different components. If the probability P_i to find a rod in any of its M orientations in the fluid is identical for $i = 1, 2, \ldots, M$ (which means that the probability, per unit solid angle, to find a given orientation is independent of direction) then the orientational entropy can be written as

$$S(\text{isotropic}) = -k_B \sum_{i=1}^{M} P_i \ln P_i = -k_B \sum_{i=1}^{M} \frac{1}{M} \ln \frac{1}{M} = k_B \ln M$$

However, if the rods are aligned, the probabilities P_i are not all the same, and hence

$$S(\text{nematic}) = -k_B \sum_{i=1}^{M} P_i \ln P_i \leq S(\text{isotropic})$$

Clearly, for hard rods orientational ordering decreases orientational entropy (the correct definition of the orientational entropy would include a term that depends on the discretization but that is irrelevant to the difference $S(\text{nematic}) - S(\text{isotropic})$). However — and this is the crux of Onsager's argument — orientational ordering increases translational entropy. To see this, one can compare the excluded volumes for two rods with diameter D and length L when constrained to be either parallel or perpendicular to each other (Fig. 1a). As the ratio of excluded volumes for the parallel and perpendicular scales as D/L, in the limit of very thin, very long rods — that is, when $D/L \to 0$ — the excluded volume for parallel rods becomes negligible. Therefore, a fluid of thin and long aligned rods behaves as an ideal gas, with an entropy per rod (for N rods in volume V) equal to $k_B \ln(V/N)$, which is a well-known result of statistical mechanics (as before, terms that are unaffected by the phase transition can be ignored). However, for N orientationally disordered rods, a given rod is excluded from a volume of the order of $O(NL^2D)$. The larger the excluded volume (or the smaller the accessible volume), the lower the translational entropy. Therefore, orientationally disordered rods can increase translational entropy by becoming more aligned — that is, at the expense of some orientational entropy. In fact, Onsager showed (see ref. 2 for a review) that translational entropy can be gained at the expense of orientational entropy only beyond a certain density.

This hand-waving discussion of Onsager's theory of the isotropic–nematic transition illustrates the key aspects of all ordering phase transitions (or for that matter, other local ordering phenomena) that are accompanied by an increase in entropy: in every single case, one type of entropy decreases and another kind of entropy increases such that the total entropy becomes larger. In other words, entropy-driven ordering is not a violation of the second law.

Another common example of entropy-driven ordering is that of the freezing of hard spheres. The first indications that a fluid of hard spheres might freeze came from numerical simulations carried out by William Wood and J. D. Jacobson[3] and by Berni Alder and Thomas Wainwright[4]. As the formation of an ordered crystal from a disordered liquid seems to be the epitome of an ordering transition, the simulations were received with much scepticism, to the extent that at a workshop in 1957[5] a panel of experts (including two Nobel laureates) were asked to vote whether they believed in the evidence for hard-sphere freezing. It was a draw; the Chair (George Uhlenbeck) then tipped the balance by voting against. Since 1957, the situation has changed drastically: not only is hard-sphere freezing now widely accepted, but there exist many theories and, more importantly, experiments[6] that provide direct evidence for the existence of a transition where hard spherical particles spontaneously freeze. What entropy trade-off makes such freezing possible? Again, it is useful to relate the entropy per particle to the logarithm of the volume accessible to that particle. For a crystalline solid, the accessible volume can be simply and

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intuitively interpreted as the space within which a particle can move without bumping into the particles sitting on adjacent lattice sites. If the crystal is densely packed, such free volume tends to zero (Johannes Kepler demonstrated that this happens when the spheres occupy a fraction $\pi/\sqrt{18}$, or about 74%, of the total volume). In the dilute fluid phase, free volume per particle is much larger (for an ideal gas it is V/N). However, as the density of the fluid is increased, free volume per particle decreases rapidly and reaches zero at the so-called random-close-packing point, which occurs at a volume fraction of about 64%. Hence, at higher densities, hard spheres must crystallize (at least in part) to gain accessible volume and thus entropy. Yet crystals are not the only ordered structures that can form on compression of a hard-sphere fluid; hard colloids can also form highly ordered icosahedral clusters that are less dense than the Kepler packing yet certainly denser than any fluid[7].

Since the early work of Onsager, Wood and Alder, entropic ordering transitions have been found to be extremely common, certainly in colloidal matter. Simulations have shown that entropic effects alone can account for a wide variety of lyotropic liquid-crystalline phases that have been observed in experiments[8]. More recently, simulations on a wide range of convex, hard polyhedral particles have demonstrated that entropy can drive the formation of a whole zoo of crystals, liquid crystals, and even quasicrystals[9].

But there are even simpler examples of phenomena where entropy plays a counterintuitive role. For example, in the mixing of colloidal particles and smaller globular polymers, the colloids and the polymers separate into two fluid phases, one containing mainly colloids, the other containing mainly polymers[10]. And this happens in the absence of attractive forces between the colloids or the polymers. The simplest description of the physics underlying this demixing phenomenon was given some 50 years ago by Sho Asakura and Fumio Oosawa[11], who showed that the purely repulsive interaction between the polymers and the colloids can induce an effective attractive interaction between the colloids (the implications of this so-called depletion interaction for colloidal demixing were first explored in 1976[12]). The Asakura–Oosawa model assumes that the polymers only interact with the colloids (that is, that the translational entropy of a pure polymer solution is that of an ideal gas), and that the polymers behave as spherical particles with radius R_P and are completely excluded from a shell with radius $R = R_P + R_C$ around the centre of each colloid with radius R_C. Rather than to work out the consequence of this model in detail (for this, see ref. 13, for example), one can consider a one-dimensional case: a mixture of colloidal rectangles and polymer disks, alternately positioned along a line (Fig. 1b). If the length available to such a mixture is shorter than the sum of the diameters of all colloid and polymer particles, the system is jammed (that is, there is absence of translational freedom). However, when the polymers and the colloids are separated, they easily fit within a length larger than the sum of the diameters of the colloids alone. This explanation, albeit simplistic, clearly illustrates that under certain conditions mixtures of hard particles can increase their entropy by demixing. The story becomes more complicated if the polymers can adsorb on the colloids[14], however.

The recurring theme in all the above examples is that virtually all phase transitions involving liquids, vapours, crystals or liquid crystals, even those transitions whose occurrence is commonly attributed to attractive energetic interactions, can be reproduced by using entropy alone. This is important because in experiments entropic interactions can be tuned: colloidal particles with a variety of shapes can be synthesized, and the size and concentration of the polymers (or other smaller colloidal particles) that cause the depletion interaction between the colloidal particles can be controlled. We thus have far greater control over the interactions between colloids than over those between small molecules. This is of crucial

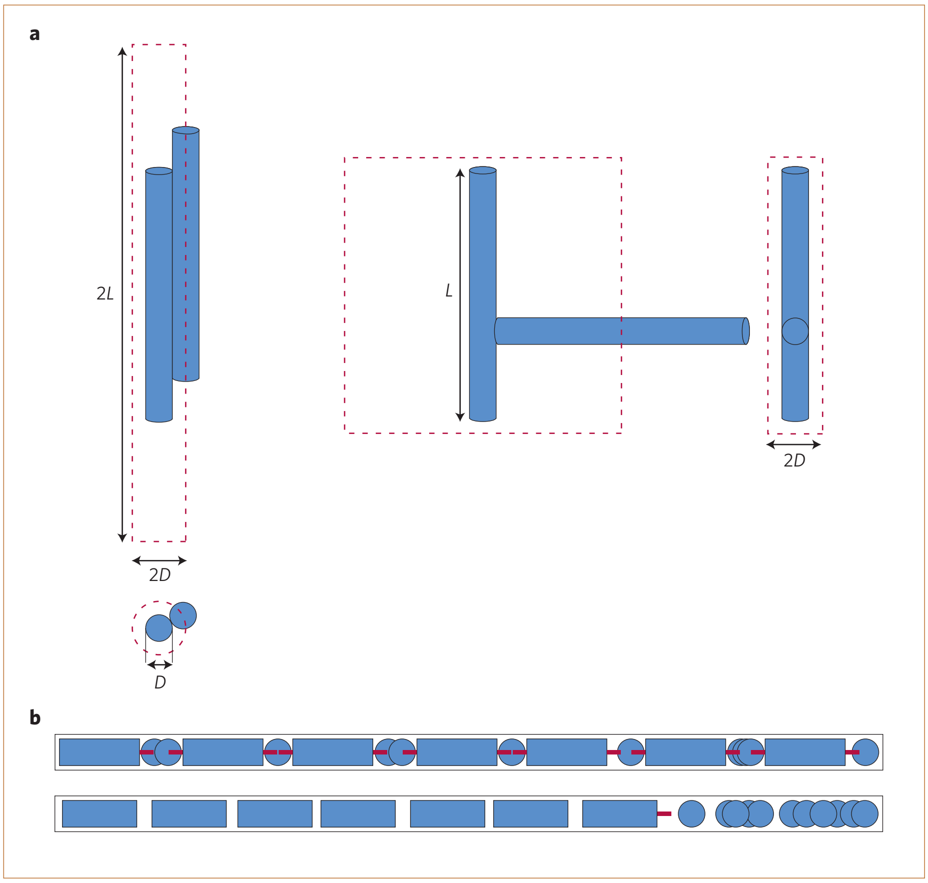

Figure 1 | Entropic forces. **a**, A rod with length L and diameter D excludes the geometrical centre of a second identical rod from occupying a certain volume (red lines). In the limit of $L \gg D$, this volume is minimal ($2\pi LD^2$) if the rods are parallel and maximal ($2L^2D$) when they are perpendicular. Hence, rod alignment maximizes translational entropy (and above a certain density, the gain in translational entropy outweighs the loss in orientational entropy). **b**, Simplified, one-dimensional example of the depletion interaction. The blue rectangles cannot overlap with each other or with the disks (that is, the centres of the disks are 'depleted' from the regions shown in red), but the disks can intersect. In this system, a configuration of alternating rectangles and disks (top) has less entropy than a system where the rectangles and disks are separated (bottom), because in the latter the particles have more freedom of motion (the total area accessible to the disks is larger).

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Figure 2 | Schematic of the self-assembly of 'DNA bricks' (each of which is a 32-base string of single-stranded DNA that can bind to four neighbouring bricks) into a complex structure where every brick is distinct and has a unique position. Figure reproduced with permission from ref. 15, © 2012 American Association for the Advancement of Science.

importance for the design of complex self-assembling structures.

Addressable complexity

Crystals, liquid crystals and quasicrystals can all form by self-assembly of tailor-made colloidal building blocks, and these can be designed so that such ordered structures increase the entropy of the system. Indeed, over the past few decades much of the research on complex self-assembly has focused on materials with structural complexity. Yet there is another form of complexity that needs to be mastered if we are ever to make complex self-assembled machines or devices consisting of many distinct building blocks, each of them located in a pre-specified position. Such 'addressable complexity' is different from that in a one-component crystal, where permutations of the building blocks do not affect the properties of the material. Instead, systems with addressable complexity can in principle self-assemble from hundreds or even thousands of distinct components, as exemplified by the self-assembly of short single-stranded 'DNA bricks' into complex finite structures in which every DNA brick occupies a predetermined position[15] (Fig. 2). Of course, the self-assembled DNA structure contains much more information than a one-component crystal. For example, there is only one way in which a structure consisting of N bricks can be assembled correctly. In contrast, in a crystal of N identical colloids there are $N!$ ways to distribute the colloids over the crystal without changing its properties. Hence, to make the DNA structure addressable, the entropic cost of the encoded information, described by the entropy per particle $s_{\text{address}} = k_B(\ln N - 1)$ assuming that $N \gg 1$, has to be 'paid' during self-assembly. Indeed, the free energy of DNA hybridization compensates for the high entropic cost of addressable self-assembly. In principle, purely entropic 'lock–key' interactions — depletion attractions between pairs of colloids of appropriately designed shape — might achieve the same (but the design of the building blocks would be nontrivial). However, because the entropic cost per (colloidal) particle (or brick) increases with N, ever-stronger specific pair interactions are needed to make increasingly larger structures with addressable complexity. Also, in these structures, nonspecific interactions between particles that should not be adjacent in the target structure should be sufficiently weak so as to be easily broken during the self-assembly process — that is, the structure must be able to anneal. The problem is that the stronger specific interactions needed to overcome the entropic cost involved in the design of larger structures almost inevitably imply the presence of stronger nonspecific interactions. If the latter become significantly larger than the thermal energy at the assembly temperature, the kinetics of self-assembly are compromised[16]. The existence of such a kinetic barrier does not necessarily mean that the design of large structures with addressable complexity is doomed. Rather, it suggests that assembly will have to follow a protocol where not all units assemble at the same time. Possible hierarchical assembly scenarios are discussed elsewhere[17]. At present, experiments to assemble complex addressable structures exploit the selective binding properties of complementary DNA strands, yet other 'ligand–receptor' pairs might be used in future provided that they exhibit similar selectivity.

It is difficult to overestimate the importance of addressable complexity: all macroscopic 'machines' consist of many distinct parts that need to be assembled into a unique spatial pattern. If addressable complexity can be developed to the point where nanoscale objects (such as metal or semiconductor nanoparticles, or molecular building blocks) can assemble spontaneously into a predetermined three-dimensional arrangement, the road is open to the design of intricate machines at the nanoscale. Yet one should always remember that natural evolution got there first: biomolecules such as proteins and RNA form complex, addressable three-dimensional structures by hierarchical design. Not surprisingly, there is a close analogy between addressable self-assembly and protein folding. The ways in which the protein-folding process is steered may thus provide inspiration for non-protein-based self-assembly. ❒

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Lagrange multiplier

From Wikipedia, the free encyclopedia

In mathematical optimization, the **method of Lagrange multipliers** (named after Joseph Louis Lagrange[1]) is a strategy for finding the local maxima and minima of a function subject to equality constraints.

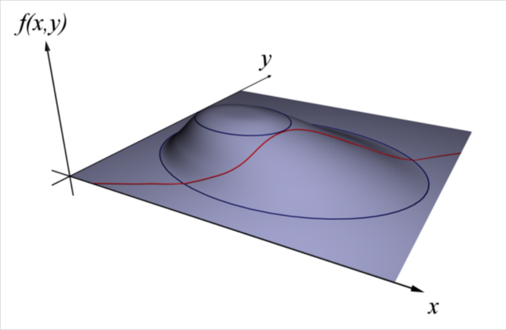

Figure 1: Find x and y to maximize $f(x, y)$ subject to a constraint (shown in red) $g(x, y) = c$.

For instance (see Figure 1), consider the optimization problem

maximize $f(x, y)$
subject to $g(x, y) = c$.

We need both f and g to have continuous first partial derivatives. We introduce a new variable (λ) called a **Lagrange multiplier** and study the **Lagrange function** (or **Lagrangian**) defined by

$$\mathcal{L}(x, y, \lambda) = f(x, y) - \lambda \cdot (g(x, y) - c),$$

where the λ term may be either added or subtracted. If $f(x_0, y_0)$ is a maximum of $f(x, y)$ for the original constrained problem, then there exists λ_0 such that (x_0, y_0, λ_0) is a stationary point for the Lagrange function (stationary points are those points where the partial derivatives of $\mathcal{L}$ are zero). However, not all stationary points yield a solution of the original problem. Thus, the method of Lagrange multipliers yields a necessary condition for optimality in constrained problems.[2][3][4][5][6] Sufficient conditions for a minimum or maximum also exist.

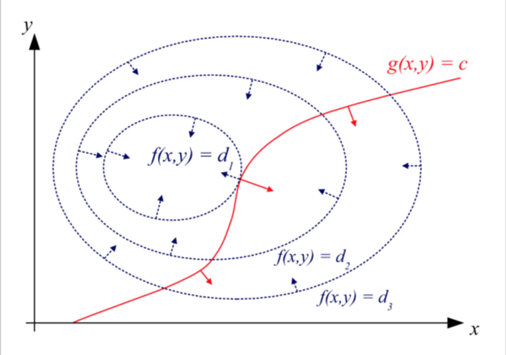

Figure 2: Contour map of Figure 1. The red line shows the constraint $g(x, y) = c$. The blue lines are contours of $f(x, y)$. The point where the red line tangentially touches a blue contour is the solution. Since $d_1 > d_2$, the solution is a maximization of $f(x, y)$.

Contents

Context and method

One of the most common problems in calculus is that of finding maxima or minima (in general, "extrema") of a function, but it is often difficult to find a closed form for the function being extremized. Such difficulties often arise when one wishes to maximize or minimize a function subject to fixed outside equality constraints. The method of Lagrange multipliers is a powerful tool for solving this class of problems without the need to explicitly solve the conditions and use them to eliminate extra variables.

Single constraint

Consider the two-dimensional problem introduced above

maximize $f(x, y)$
subject to $g(x, y) = 0$.

The method of Lagrange multipliers relies on the intuition that at a maximum, $f(x, y)$ cannot be increasing in the direction of any neighboring point where $g = 0$. If it were, we could walk along $g = 0$ to get higher, meaning that the starting point wasn't actually the maximum.

We can visualize contours of f given by $f(x, y) = d$ for various values of d, and the contour of g given by $g(x, y) = 0$.

Suppose we walk along the contour line with $g = 0$. We are interested in finding points where f does not change as we walk, since these points might be maxima. There are two ways this could happen: First, we could be following a contour line of f, since by definition f does not change as we walk along its contour lines. This would mean that the contour lines of f and g are parallel here. The second possibility is that we have reached a "level" part of f, meaning that f does not change in any direction.

To check the first possibility, notice that since the gradient of a function is perpendicular to the contour lines, the contour lines of f and g are parallel if and only if the gradients of f and g are parallel. Thus we want points (x, y) where $g(x, y) = 0$ and

$$\nabla_{x,y} f = \lambda \nabla_{x,y} g,$$

for some λ

where

$$\nabla_{x,y} f = \left(\frac{\partial f}{\partial x}, \frac{\partial f}{\partial y} \right), \qquad \nabla_{x,y} g = \left(\frac{\partial g}{\partial x}, \frac{\partial g}{\partial y} \right).$$

are the respective gradients. The constant λ is required because although the two gradient vectors are parallel, the magnitudes of the gradient vectors are generally not equal. This constant is called the Lagrange multiplier. (In some conventions λ is preceded by a minus sign).

Notice that this method also solves the second possibility: if f is level, then its gradient is zero, and setting $\lambda = 0$ is a solution regardless of g.

To incorporate these conditions into one equation, we introduce an auxiliary function

$$\mathcal{L}(x, y, \lambda) = f(x, y) - \lambda \cdot g(x, y),$$

and solve

$$\nabla_{x,y,\lambda} \mathcal{L}(x, y, \lambda) = 0.$$

Note that this amounts to solving three equations in three unknowns. This is the method of Lagrange multipliers. Note that $\nabla_{\lambda} \mathcal{L}(x, y, \lambda) = 0$ implies $g(x, y) = 0$. To summarize

$$\nabla_{x,y,\lambda} \mathcal{L}(x, y, \lambda) = 0 \iff \begin{cases} \nabla_{x,y} f(x, y) = \lambda \nabla_{x,y} g(x, y) \\ g(x, y) = 0 \end{cases}$$

The method generalizes readily to functions on n variables

$$\nabla_{x_1, \ldots, x_n, \lambda} \mathcal{L}(x_1, \ldots, x_n, \lambda) = 0$$

which amounts to solving $n + 1$ equations in $n + 1$ unknowns.