
PHASE BEHAVIOR OF LYOTROPIC LIQUID CRYSTALS

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Abstract. In these lectures, I discuss techniques to compute the phase diagram of lyotropic liquid crystals. I review the standard techniques to compute the free-energy of various phases. Subsequently, I focus on phase transitions in liquid crystals. Recent techniques to determine the dependence of phase boundaries on the shape and flexibility of the constituent molecules, are discussed. Finally, I devote attention to Monte Carlo techniques that are particularly suited to study the phase behavior of flexible molecules.

1. Introduction

These lectures focus on some of the technical aspects of the simulation of lyotropic liquid crystals. First, I review several techniques that can be used to locate first-order phase transitions. The availability of such techniques is of particular relevance for liquid-crystal simulations because many of the standard techniques to study phase-coexistence in computer simulations of simple atomic or molecular systems cannot be applied to liquid crystals. A key quantity that must be computed in order to determine the point where two phases coexist, is the chemical potential μ of the molecules in either phase. Most techniques to compute the chemical potential are limited to model systems consisting of small molecules at low densities. Actual liquid-crystal formers (both thermotropic and lyotropic) rarely meet this specification. I shall therefore also discuss techniques to study systems consisting of large, flexible molecules.

2. Phase transitions and free energy

The most direct way to study phase coexistence in a computer simulation would be to simply change the temperature or pressure of the system under study until a phase transformation occurs. In the real world it is often (but by no means always) possible to ensure that such a phase change takes place reversibly. The coexistence point is defined as the point where the reversible phase transformation occurs. At coexistence, the temperature and pressure of the coexisting phases are equal. In addition, the chemical potential of every individual species must have the same value in every phase. Following the seminal work of Panagiotopoulos [1], much progress has been made in the direct simulation of phase coexistence of moderately dense fluid phases using the "Gibbs-ensemble" method. This method relies on the fact that it is possible to satisfy the above conditions for coexistence between two bulk phases (or, to be more precise, homogeneous phases with periodic boundary conditions) by allowing them to exchange both volume and molecules. Unfortunately, such a direct simulation method is of limited value in computer simulations of transitions involving dense phases that have some translational order. The reason why the Gibbs-ensemble method breaks down under those circumstances is twofold. First of all, pronounced hysteresis effects are usually observed in computer simulations of a strong first order phase transition, such as melting. This implies that it is difficult for the molecules in the system to spontaneously rearrange from a configuration belonging to the 'old' phase, to one that corresponds to the 'new' phase. But even if the two different phases have somehow been prepared, it is usually impossible to exchange particles between them. As a consequence, we cannot ensure the equality of the chemical potential in the two phases.

Under those circumstances, it is still possible to locate the point where the two phases coexist. But in order to do so, we must explicitly compute the chemical potential of the homogeneous phases at the same temperature and pressure and find the point where the two μ 's are equal. The direct calculation of chemical potentials of dense phases is the first topic that I address in these lectures. In practice, it is often the Helmholtz free energy F , rather than the chemical potential μ , that is computed. In what follows, I shall use the terms chemical-potential calculations and free-energy calculations interchangeably, as F and μ are simply related (e.g., for a one-component system of N particles in a volume V at pressure P , we have $F = N\mu - PV$).

2.0.1. *The natural way*

When discussing techniques to measure free energies, it is useful to recall how such quantities are measured experimentally. In the real world, free

energies cannot be obtained from a single measurement either. What can be measured, however, is the derivative of the free energy with respect to volume V and temperature T :

$$\left(\frac{\partial F}{\partial V}\right)_{NT} = -P \quad (1)$$

and

$$\left(\frac{\partial F/T}{\partial 1/T}\right)_{NV} = E. \quad (2)$$

Here P is the pressure and E the energy of the system under consideration. The trick is now to find a reversible path that links the state under consideration to a state of known free energy. The change in F along that path can then simply be evaluated by integration of Eqns. 1 and 2. In the real world the free energy of a substance can only be evaluated directly for a very limited number of thermodynamic states. One such state is the ideal gas phase, the other is the perfectly ordered ground state at $T = 0K$. In computer simulations, the situation is quite similar. In order to compute the free energy of a dense liquid, one may construct a reversible path to the very dilute gas phase. It is not really necessary to go all the way to the ideal gas. But at least one should reach a state that is sufficiently dilute that the free energy can be computed accurately, either from knowledge of the first few terms in the virial expansion of the compressibility factor $PV/Nk_B T$, or that the chemical potential can be computed by other means (see below). For the solid, the ideal gas reference state is less useful (although techniques have been developed to construct a reversible path from a dense solid to a dilute (lattice-) gas [2]). The obvious reference state for solids is the harmonic lattice. Computing the absolute free energy of a harmonic solid is relatively straightforward, at least for atomic and simple molecular solids. However, not all solid phases can be reached by a reversible route from a harmonic reference state. For instance, in molecular systems it is quite common to find a strongly an-harmonic plastic phase just below the melting line. This plastic phase is not (meta-) stable at low temperatures.

2.0.2. *Artificial reversible paths*

Fortunately, in computer simulations we do not have to rely on the presence of a 'natural' reversible path between the phase under study and a reference state of known free energy. If such a path does not exist, we can construct an artificial path. This is in fact a standard trick in statistical mechanics (see e.g. [3]). It works as follows: Consider a case where we need to know the free energy $F(V, T)$ of a system with a potential energy function U_1 , where U_1 is such that no 'natural' reversible path exists to a state of known free energy. Suppose now that we can find another model system with a

potential energy function U_0 for which the free energy *can* be computed exactly. Now let us define a generalized potential energy function $U(\lambda)$, such that $U(\lambda = 0) = U_0$ and $U(\lambda = 1) = U_1$. The free energy of a system with this generalized potential is denoted by $F(\lambda)$. Although $F(\lambda)$ itself cannot be measured directly in a simulation, we can measure its derivative with respect to λ :

$$\left(\frac{\partial F}{\partial \lambda}\right)_{NVT\lambda} = \left\langle \frac{\partial U(\lambda)}{\partial \lambda} \right\rangle_{NVT\lambda}. \quad (3)$$

If the path from $\lambda = 0$ to $\lambda = 1$ is reversible, we can use Eqn. 3 to compute the desired $F(V, T)$. We simply measure $\langle \partial U / \partial \lambda \rangle$ for a number of values of λ between 0 and 1. Typically, 10 quadrature points will be sufficient to get the absolute free energy per particle accurate to within $0.01 k_B T$. It is however important to select a reasonable reference system. One of the safest approaches is to choose as a reference system an Einstein crystal with the same structure as the phase under study [4]. This choice of reference system makes it extremely improbable that the path connecting $\lambda = 0$ and $\lambda = 1$ will cross an (irreversible) first order phase transition from the initial structure to another, only to go back to its original structure for still larger values of λ . Nevertheless, it is important that the parametrization of $U(\lambda)$ be chosen carefully. Usually, a linear parametrization (i.e. $U(\lambda) = \lambda U_1 + (1-\lambda)U_0$) is quite satisfactory. But occasionally such a parametrization may lead to weak (and relatively harmless) singularities in Eqn. 3 for $\lambda \rightarrow 0$. More details about such free energy computations can be found in refs. [5, 6].

2.1. PHASE TRANSITIONS IN LIQUID CRYSTALS

2.1.1. *Isotropic and nematic phases*

For the isotropic phase we can take the ideal gas as a reference and integrate along the equation of state using the density ρ as the integration parameter

$$\frac{F(\rho, L)}{Nk_B T} - \frac{F_{id}(\rho)}{Nk_B T} = \int_0^\rho \frac{P(\rho', L) - \rho' k_B T}{\rho'^2 k_B T} d\rho'. \quad (4)$$

The isotropic-nematic transition usually exhibits some hysteresis. As a consequence, direct integration of the equation of state through the transition region is subject to statistical errors. This problem can be alleviated by switching on a strong ordering field. In the presence of such a field, the first-order isotropic-nematic transition is suppressed and a reversible expansion to the dilute gas becomes possible [7].

A second method that can be used to compute the free energy of the nematic phase is based on the particle-insertion method of Widom [8]. This

method was first applied to the evaluation of the free energy of nematics by Eppenga and Frenkel [9]. As I shall discuss particle-insertion schemes in some detail below, I defer the discussion of this technique to section 4.1. Suffice it to say that this scheme works best for strongly anisometric molecules that undergo a transition to the nematic phase at low density.

2.1.2. *Solid phase*

The strong first order transition separating the solid phase from the other phases rules out the integration along the equation of state. Instead, we choose as reference system for the solid an Einstein crystal with the same structure [4]. Now the reversible path transforms the original system to an Einstein crystal with fixed center-of-mass, by gradually coupling the atoms to their equilibrium lattice position. For a system of anisometric particles, the orientation also needs to be coupled to an aligning field. The Hamiltonian that can be used to achieve the coupling is

$$\beta H_{\mu,\lambda} = \mu \sum_i (\mathbf{r}_i - \mathbf{r}_i^0)^2 + \lambda \sum_i \sin^2 \theta_i, \quad (5)$$

where μ and λ are the coupling constants which determine the strength of the harmonic forces. The free energy of the system can be related to the (known) free energy of an Einstein crystal by thermodynamic integration

$$\frac{\beta F(\rho^*)}{N} = \frac{\beta F_{ein}}{N} - \int_0^{\mu_{max}} d\mu \langle \Delta r^2 \rangle_\mu - \int_0^{\lambda_{max}} d\lambda \langle \sin^2 \theta \rangle_\lambda - \frac{\ln V}{N}. \quad (6)$$

Here $\langle \Delta r^2 \rangle_\mu$ is the mean-square displacement and $\langle \sin^2 \theta \rangle_\lambda$ the mean square sine of the angle between a particle and the aligning field in a simulation with Hamiltonian $H_{\mu,\lambda}$. The free energy of the Einstein crystal (with fixed center-of-mass) in the limit of large coupling constants is given by

$$\beta F_{ein} = \frac{3}{2} \ln N - \frac{3}{2} (N-1) \ln \frac{\pi}{\mu} - N \ln \frac{2\pi}{\lambda}. \quad (7)$$

By performing several simulations at different values of μ and λ one can numerically evaluate the integrals in Eqn. 6. As the values μ and λ at which the integrand is evaluated can be chosen freely, the error in the integration can be minimized by using Gauss-Legendre quadrature. Occurrence of any first order transition was avoided by performing two Gauss-Legendre integrations in succession. The first fixes the positions while leaving $\lambda = 0$, the second aligns all spherocylinders while keeping $\mu = \mu_{max}$. It is convenient to choose the maximum values of λ and μ such that in a simulation at these maximum values, there are essentially no overlaps between the particles. Otherwise it is necessary to correct Eqn. 7 for the occurrence of overlaps [4].

2.1.3. Smectic phase

The smectic phase does not have an obvious reference state for which the free energy is known. In the case of hard spherocylinders, Veerman and Frenkel [10] used the fully aligned system as a reference system. However, the free energy of the aligned parallel smectic itself is subject to numerical error. An alternative is to couple the mesogenic molecules with an harmonic spring to the smectic layer to which they belong and subsequently align them. In this way, the smectic phase of hard spherocylinders can be transformed into what is essentially a 2D hard disk fluid for which the free energy is well known [2]. In principle, one could apply the Einstein integration method used in the previous section with one difference: the position field couples only the z -coordinates of the particles to the layer positions and leaves the x, y coordinates completely free. If we consider the first part of the integration, where the particles are confined to their layers, the free energy of smectic phase can be related to this planar system by

$$\frac{\beta F_{\mu=0}}{N} = \frac{\beta F_{\mu=\mu_0}^{\text{planar}}}{N} - \int_0^{\mu_0} d\mu \langle \Delta r^2 \rangle_{\mu} - \frac{\ln V}{N}. \quad (8)$$

In the second integration, the difficulty arises that a infinite amount of aligning energy is needed to get all spherocylinders completely parallel.

$$\frac{\beta F_{\lambda=0, \mu=\mu_0}^{\text{planar}}}{N} = \frac{\beta F_{\lambda=\infty, \mu=\mu_0}^{\text{planar, aligned}}}{N} - \int_0^{\infty} d\lambda \langle \sin^2 \theta \rangle_{\lambda}. \quad (9)$$

To keep the energy values finite, we subtract on both sides of this equation the free energy of an ideal rotator in the same field.

$$\frac{\beta F_{\lambda=\lambda_0, \mu=\mu_0}^{\text{planar, id}}}{N} = \frac{\beta F_{\lambda=\infty, \mu=\mu_0}^{\text{planar, aligned, id}}}{N} - \int_{\lambda_0}^{\infty} d\lambda \langle \sin^2 \theta \rangle_{\text{id}, \lambda} \quad (10)$$

which results in

$$\begin{aligned} \frac{\beta F_{\lambda=0, \mu=\mu_0}^{\text{planar}}}{N} &= \frac{\beta F_{\lambda=\lambda_0, \mu=\mu_0}^{\text{planar, id}}}{N} + \frac{\beta F_{\lambda=\infty, \mu=\mu_0}^{\text{planar, aligned, ex}}}{N} \\ &\quad - \int_0^{\lambda_0} d\lambda \langle \sin^2 \theta \rangle_{\lambda} - \int_{\lambda_0}^{\infty} d\lambda \left[\langle \sin^2 \theta \rangle_{\lambda} - \langle \sin^2 \theta \rangle_{\text{id}, \lambda} \right]. \end{aligned} \quad (11)$$

The excess free energy of the completely aligned planar system, that is $\beta F_{\lambda=\infty, \mu=\mu_0}^{\text{planar, aligned, ex}}$, is equal to the excess free energy of a 2D hard disk fluid. The free energy of the ideal planar system (with fixed center-of-mass) in the limit of large coupling constants is given by

$$\beta F_{\lambda=\lambda_0, \mu=\mu_0}^{\text{planar, id}} = \frac{1}{2} \ln N - \frac{1}{2} (N-1) \ln \frac{\pi}{\mu} - N \ln \frac{2\pi}{\lambda}. \quad (12)$$

The integral over the difference of the \sin^2 terms in Eqn. 11 is finite. We can change the integration boundaries by substituting $\lambda = 1/\xi^2$.

$$\int_{\lambda_0}^{\infty} d\lambda \left[\langle \sin^2 \theta \rangle_{\lambda} - \langle \sin^2 \theta \rangle_{id,\lambda} \right] = \int_0^{\frac{1}{\sqrt{\lambda_0}}} d\xi 2\lambda^{\frac{2}{3}} \left[\langle \sin^2 \theta \rangle_{\lambda} - \langle \sin^2 \theta \rangle_{id,\lambda} \right]. \quad (13)$$

In conventional MC sampling, the statistical error of both terms in the integrand is larger than the difference itself. Under those circumstances, the following approach is useful: instead of rotating a spherocylinder i around an angle $d\theta_i$ we choose a completely new trial value of θ_i from the probability distribution

$$P(\theta) \sim \exp(-\beta\lambda \sin^2 \theta). \quad (14)$$

This is the equilibrium distribution for an ideal rotator with a Hamiltonian according to Eqn. 5 and results in the correct value for $\langle \sin^2 \theta \rangle_{id,\lambda}$. If no overlap occurs the trial move will be accepted and we will have

$$\sin_{\lambda}^2 \theta_i - \sin_{id,\lambda}^2 \theta_i = 0. \quad (15)$$

If an overlap does occur the trial move will be rejected and the particle will retain its old value. The difference now will be

$$\sin_{\lambda}^2 \theta_i - \sin_{id,\lambda}^2 \theta_i = \sin_{\lambda}^2 \theta_i^{old} - \sin_{id,\lambda}^2 \theta_i^{new}. \quad (16)$$

The statistical error in the average of the difference is always smaller than the average itself. This will enable us to determine the integrand more accurately. By combining Eqns. 8,11 and 13 the complete expression for free energy of the smectic phase follows

$$\begin{aligned} \frac{\beta F_{\mu=0}}{N} &= \frac{\beta F_{disk}^{ex}}{N} - \frac{\beta F_{\lambda=\lambda_0, \mu=\mu_0}^{planar,id}}{N} - \frac{\ln V}{N} - \int_0^{\mu_0} d\mu \langle \Delta r^2 \rangle_{\mu} \\ &\quad - \int_0^{\lambda_0} d\lambda \langle \sin^2 \theta \rangle_{\lambda} - \int_0^{\frac{1}{\sqrt{\lambda_0}}} d\xi 2\lambda^{\frac{2}{3}} \left[\langle \sin_{\lambda}^2 \theta - \sin_{id,\lambda}^2 \theta \rangle \right]. \end{aligned} \quad (17)$$

The excess hard disk free energy can be obtained by subtracting the ideal term $\beta F_{disk}^{id} = \ln \rho$ from the free energy in Ref [2]. Another problem that may arise is that, as the smectic phase forms from the nematic, the fluctuations in the number of particles per layer get frozen in. As a result, different layers may have different (2D) densities. To ensure that the 2D densities in the smectic layers are equal throughout the system one can use shifted periodic boundaries: the periodic boundaries in the x direction are shifted exactly one layer period along the z -axis, while leaving them the same in the y and z direction. In this way, a particle leaving the simulation

box at the left side will reenter the box at the right *one layer higher*. This particle can diffuse through the whole system, as there is effectively only one layer. This ensures that fluctuations in the number of particles per smectic layer can relax, even at high density where normal inter-layer diffusion is completely frozen out [11].

2.1.4. Nematic-smectic free energy difference

Even when all tricks to compute the absolute free energies of the different phases are used, it remains difficult to locate the nematic-smectic coexistence region with reasonable accuracy. However, we are hardly ever interested in the absolute free energies themselves. It is often attractive to calculate the free energy difference between a stable nematic and a stable smectic directly. In order to find a reversible path from the nematic to smectic one can use the following Hamiltonian

$$H_\lambda = \lambda \left(\sum_i \cos\left(\frac{2\pi n r_{i,z}}{L_z}\right) + 1 \right), \quad (18)$$

where n is the number of smectic layers, L_z the box length in the z -direction, $r_{i,z}$ the z -coordinate of particle i and λ the coupling parameter determining the strength of the smectic ordering. At low density this Hamiltonian will produce, by increasing λ , a gradual transition from a nematic to a smectic phase. We start with a smectic phase and applied a cosine field at large enough λ . Subsequently, the smectic is expanded to lower density, while measuring the pressure. Finally, the cosine field is slowly turned off. The free energy difference now simply is

$$\begin{aligned} \frac{\Delta F_{ns}}{N} &= \frac{F_{smec}}{N} - \frac{F_{nem}}{N} = \int_0^{\lambda_{max}} d\lambda \left\langle \sum_i \cos\left(\frac{2\pi n r_{i,z}}{L_z}\right) + 1 \right\rangle_{smec} \\ &\quad - \int_{\rho_n}^{\rho_s} \frac{P(\rho)}{\rho^2} d\rho - \int_0^{\lambda_{max}} d\lambda \left\langle \sum_i \cos\left(\frac{2\pi n r_{i,z}}{L_z}\right) + 1 \right\rangle_{nem}. \end{aligned} \quad (19)$$

Of course, the value of λ_{max} should be chosen large enough that the first-order S-N transition is completely suppressed. For more details, see ref. [11]

2.1.5. Changing the particle shape

Usually, we are interested in the phase diagram of a model system, for a whole range of model parameters. In the case of spherocylinders, the relevant parameter is the length-to-width ratio L/D (strictly speaking, L is the length of the cylindrical part – the total length is $L + D$). Once the free energy of a phase for a given value of L/D has been determined at some density ρ , the free energy at other values of L/D can be obtained by a

simple thermodynamic integration scheme. We can compute the reversible work involved in changing the aspect ratio of the spherocylinders from L_0 to L and subsequently changing the density from ρ_0 to ρ (for convenience, we have chosen $D = 1$):

$$\frac{F(\rho, L)}{N} = \frac{F_0(\rho_0, L_0)}{N} + \int_{L_0}^L \left(\frac{\partial F}{\partial L} \right)_{\rho_0} dL + \int_{\rho_0}^{\rho} \frac{P(\rho, L)}{\rho^2} d\rho. \quad (20)$$

The pressure is obtained from an MD simulation in the usual way, by time averaging the virial.

$$\frac{\beta P}{\rho} - 1 = \frac{1}{3} \beta \sum_{i < j} \langle \mathbf{f}_{ij} \cdot \mathbf{r}_{ij} \rangle, \quad (21)$$

where r_{ij} is the vector joining the centers of mass of particles i and j , and f_{ij} denotes the (impulsive) force on j due to i . The derivative $\kappa = (\partial F / \partial L)_{\rho}$ can be measured at the same time by taking the projection of the intermolecular force along the particle axis.

$$\kappa = \left(\frac{\partial F}{\partial L} \right)_{\rho} = \frac{1}{2} \sum_{ij} \langle \mathbf{f}_{ij} \cdot (\mathbf{u}_i + \mathbf{u}_j) \rangle. \quad (22)$$

The average κ is calculated at constant number density ρ . However, it is more convenient to measure it at constant reduced density ρ^* (i.e. at a constant fraction of the close-packing density). If we denote this derivative by κ' , we get

$$\kappa' = \left(\frac{\partial F}{\partial L} \right)_{\rho^*} = \left(\frac{\partial F}{\partial L} \right)_{\rho} + \left(\frac{\partial F}{\partial \rho} \right)_L \left(\frac{\partial \rho}{\partial L} \right)_{\rho^*} = \left(\frac{\partial F}{\partial L} \right)_{\rho} - \frac{\sqrt{3}}{2\rho^*} P(\rho^*, L) \quad (23)$$

and Eqn. 20 becomes

$$\frac{F(\rho^*, L)}{N} = \frac{F_0(\rho_0, L_0)}{N} + \int_{L_0}^L dL \left(\left(\frac{\partial F}{\partial L} \right)_{\rho} - \frac{\sqrt{3}}{2\rho^*} P(\rho^*, L) \right) dL + \int_{\rho_0}^{\rho^*} \frac{1}{\rho_{cp}(L)} \frac{P(\rho^*, L)}{\rho^{*2}} d\rho^*. \quad (24)$$

2.2. GIBBS-DUHEM INTEGRATION

The location of a fluid-solid coexistence curve can be determined by performing several free-energy calculations and measurements of the equation-of-state for a large number of L/D values. However, this approach is computationally rather expensive. To avoid this problem, we use a modification

of a method that was recently developed by Kofke to trace coexistence curves [12]. The advantage of this method is that only equation-of-state information *at the coexistence curve* is required to follow the L/D -dependence of the melting curve. In its original form, the Kofke scheme is based on the Clapeyron equation which describes the temperature-dependence of the pressure at which two phases coexist:

$$\frac{dP}{dT} = \frac{\Delta H}{T\Delta V}, \quad (25)$$

where ΔH is the molar enthalpy difference and ΔV the molar volume difference of the two phases. This equation is not self starting, in the sense that one point on the coexistence curve must be known before the rest of the curve can be computed by integration of Eqn. 25.

For hard-core systems, we are not interested in the (trivial) temperature dependence of the coexistence curve, but in the dependence of the coexistence pressure on L/D , the shape anisotropy of the spherocylinders. In order to obtain a Clapeyron-like equation relating the coexistence pressure to L/D , we should first write down the explicit dependence of the (Gibbs) free energy of the system on L/D :

$$dG = N\mu = VdP + \kappa dL, \quad (26)$$

where κ is the derivative $(\partial F/\partial L)_p$ defined in Eqn. 22 and where we have used the fact that D is our unit of length. Along the coexistence curve, the difference in chemical potential of the two phases is always equal to zero. Hence,

$$\Delta\mu = \Delta v dP + \frac{1}{N}\Delta\kappa dL = 0, \quad (27)$$

where Δv is the difference in molar volume of the two phases at coexistence and $\Delta\kappa = \kappa_1 - \kappa_2$. From Eqn. 27 we can immediately deduce the equivalent of the Clausius-Clapeyron equation

$$\frac{dP}{dL} = -\frac{1}{N} \frac{\Delta\kappa}{\Delta v}. \quad (28)$$

In Kofke's application of the Gibbs-Duhem method, the MC simulations are carried out in the isothermal-isobaric (NPT) ensemble. However, in the present case (hard-core particles), it is more efficient to use Molecular Dynamics to compute the derivative κ . In practice, we use a hybrid approach where MD simulations are embedded in a constant NPT-MC scheme. True constant-pressure MD is not an attractive option for hard-core models.

3. Simulations at infinite aspect ratio

3.1. SCALING

Most theoretical information about lyotropic liquid crystals has been obtained in the limit of infinite aspect ratio. Clearly, it would be interesting to perform simulations in the same limit. At first sight this seems impossible because in general the system size scales with L^3 . However, at finite reduced density ρ^* , i.e. not in the isotropic phase or low ρ^* nematic phase, the average angle θ that a particle makes with the director scales as $1/L$, which means that the particles are (almost) completely aligned. In this regime, we can bring the volume down to finite sizes by scaling the system along the director (chosen to be along the z -axis) with a factor L [11]. This will change the shape of the particle from a spherocylinder to a shifted cylinder of height 1 and diameter D . The height of the cylinder is always 1 because the angle $\theta \propto 1/L$ and the difference in height $1 - \cos(1/L) \approx 1/L^2$ vanishes as $L/D \rightarrow \infty$. The shift of the cylinder in the xy plane perpendicular to the director is finite because it is given by $L \sin \theta = \mathcal{O}(D)$ in the limit $L/D \rightarrow \infty$. The top and bottom end of the cylinder are flat and always perpendicular to the director. The hemispheres of the spherocylinder have completely disappeared by the scaling procedure.

Because the shape of the particle is different from a spherocylinder we need a new overlap criterion. This is given by the shortest distance between two particle axes in the xy plane. In the xy plane a cut through the cylinder results in a circle of diameter D . Therefore, if the shortest distance is smaller than the diameter D , an overlap will occur.

Scaling of the box in this particular way will not effect the reduced density because the close packing density will scale in the same way as the number density. The pressure will be multiplied by a factor L , whereas P/ρ remains unaffected by the scaling. We can therefore measure the equation of state in this limit using normal NPT-MC simulations.

Because the particles are free to shift any arbitrary amount in the xy plane it is convenient to keep the nematic director always along the z -axis. That is, we keep the total amount of shift in the xy plane equal to zero. This can be achieved by starting with a completely aligned system and shift two particles with the same amount in opposite direction at every MC trial move. In order to avoid multiple overlaps, shifts larger than half the box-length are forbidden. Standard MC trial moves are not very effective in reproducing the collective motion of tilted layers. In the smectic phase, we therefore allowed for two neighboring layers to tilt collectively by equal but opposite amounts, so that the constraint of a constant director is satisfied.

A similar scaling technique can be (and has been [13]) applied to oblate hard particles. In this case, the method can be used to study the nematic,

columnar and crystalline phases of disklike particles.

3.2. MIXTURES

Almost all liquid crystals of practical interest are mixtures. Either mixtures of different mesogenic molecules, or mixtures of a mesogenic and non-mesogenic molecules. In simulations, the fact that we deal with mixtures, rather than pure compounds, poses no special problems. For instance, Camp et al. [14] have studied the phase diagram of mixtures of prolate and oblate ellipsoids. The simulations reveal the presence of an isotropic phase, two nematics and one biaxial nematic.

An example of a simulation of a mixture of a mesogen and a non-mesogen is the work by Bolhuis et al. [15] on mixtures of hard spherocylinders and polymers. In this case, the presence of the polymers leads to the appearance of fluid-fluid phase transitions in the various liquid-crystalline phases.

More interesting from a technical point of view are simulations of mixtures of particles with a continuous size or shape distribution. The general approach in this case is discussed in a paper by Bolhuis and Kofke, who studied the freezing of polydisperse hard-sphere mixtures [16]. This approach was extended to polydisperse lyotropic liquid crystals by Bates and Frenkel [17]. The interesting point is that, in this case, poly-dispersity may induce phases that are absent in the phase diagram of mono-disperse particles. For example: mono-disperse spherocylinders do not exhibit a columnar phase, but polydisperse spherocylinders do.

4. Chemical potential of flexible molecules

Before discussing techniques to measure the chemical potential of chain molecules, I first review the particle-insertion method of Widom [8].

4.1. THE PARTICLE INSERTION METHOD

A particularly simple and elegant method to measure the chemical potential μ of a species in a pure fluid or in a mixture is the 'particle-insertion' method (often referred to as the Widom-method [8]). The statistical mechanics that is the basis for this method is quite simple. Consider the definition of the chemical potential μ_α of a species α . From thermodynamics we know that μ is defined as:

$$\mu = \left(\frac{\partial G}{\partial N} \right)_{PT}$$

$$\begin{aligned}
&= \left(\frac{\partial F}{\partial N} \right)_{VT} \\
&= -T \left(\frac{\partial S}{\partial N} \right)_{VE} .
\end{aligned} \tag{29}$$

Where G , F and S are the Gibbs free energy, the Helmholtz free energy and the entropy, respectively. Here, and in the next few paragraphs we focus on a one-component system, and hence we drop the subscript α . Let us first consider the situation at constant NVT . If we express the Helmholtz free energy of an N -particle system in terms of the partition function Q_N

$$\begin{aligned}
F(N, V, T) &= -k_B T \ln Q_N \\
&= -k_B T \ln \left(\frac{(q(T)V)^N}{N!} \right) - k_B T \ln \left(\int ds^N \exp[-\beta U(\mathbf{s}^N; L)] \right) \\
&= F_{id}(N, V, T) + F_{ex}(N, V, T) ,
\end{aligned} \tag{30}$$

then it is obvious from Eqn. 29 that, for sufficiently large N the chemical potential is given by: $\mu = -k_B T \ln(Q_{N+1}/Q_N)$. If we use the explicit form (Eqn. 30) for Q_N , we find:

$$\begin{aligned}
\mu &= -k_B T \ln(Q_{N+1}/Q_N) \\
&= -k_B T \ln \left(\frac{qV}{(N+1)} \right) - k_B T \ln \left(\frac{\int ds^{N+1} \exp(-\beta U(\mathbf{s}^{N+1}))}{\int ds^N \exp(-\beta U(\mathbf{s}^N))} \right) \\
&= \mu_{id}(V) + \mu_{ex} .
\end{aligned} \tag{31}$$

In the first line of Eqn. 31, we have assumed that the system is contained in a cubic box with diameter $L = V^{1/3}$ and have defined scaled coordinates \mathbf{s}^N , by:

$$\mathbf{q}_i = L\mathbf{s}_i$$

for $i = 1, 2, \dots, N$. In the last line of Eqn. 31, we have indicated the separation in the ideal-gas contribution to the chemical potential, and the excess part. As $\mu_{id}(V)$ can be evaluated analytically, we focus on μ_{ex} . We now separate the potential energy of the $N+1$ -particle system into the potential energy function of the N -particle system, $U(\mathbf{s}^N)$, and the interaction energy of the $N+1$ -th particle with the rest: $\Delta U \equiv U(\mathbf{s}^{N+1}) - U(\mathbf{s}^N)$. Using this separation, we can write μ_{ex} as:

$$\mu_{ex} = -k_B T \ln \langle \int ds_{N+1} \exp(-\beta \Delta U) \rangle_N , \tag{32}$$

where $\langle \dots \rangle_N$ denotes canonical ensemble averaging over the configuration space of the N -particle system. The important point to note is that

where $\langle \dots \rangle_N$ denotes canonical ensemble averaging over the configuration space of the N -particle system. The important point to note is that equation 32 expresses μ_{ex} as an ensemble average that can be sampled by the conventional Metropolis scheme [18]. There is only one aspect of this equation that makes it different from the averages that we considered before, namely the fact that we compute the average of an *integral* over the position of particle $N + 1$. This last integral can be sampled by brute-force (unweighted) Monte Carlo sampling. In practice the procedure is as follows: we carry out a perfectly normal constant- NVT Monte Carlo simulation on the system of N particles. At frequent intervals during this simulation (for instance, after every MC trial move) we randomly generate a coordinate \mathbf{s}_{N+1} , uniformly over the unit cube. With this value of \mathbf{s}_{N+1} , we then compute $\exp(-\beta\Delta U)$. By averaging the latter quantity over all generated trial positions, we obtain the average that appears in Eqn. 32. So, in effect, we are computing the average of the Boltzmann factor associated with the random insertion of an additional particle in an N -particle system, *but we never accept any such trial insertions*, because then we would no longer be sampling the average needed in Eqn. 32. The Widom method provides us with a very powerful scheme to compute the chemical potential of (not too dense) atomic and simple molecular liquids.

The particle insertion scheme fails when the probability of 'accepting' a trial insertion becomes very small. One consequence is that the simple particle insertion method is less suited for molecular than for atomic systems. This is so because the probability of accepting the random trial insertion of a large molecule in a fluid is usually extremely small.

4.2. CHEMICAL POTENTIAL OF MACRO-MOLECULES WITH DISCRETE CONFORMATIONS

In order to understand the methods that have been devised to calculate the chemical potential of chain molecules, it is instructive to first consider how we would compute μ_{ex} of a chain molecule with the Widom technique. To this end, I introduce the following notation: the position of the first segment of the chain molecule is denoted by \mathbf{q} and the conformation of the molecule is described by Γ . The configurational part of the partition function of a system of chain molecules can be written as

$$Q_{chain}(N, V, T) = \frac{1}{N!} \int d\mathbf{q}^N \sum_{\Gamma_1, \dots, \Gamma_n} \exp(-\beta U(\mathbf{q}^N, \Gamma^N)). \quad (33)$$

where of the $Q(N+1, V, T)$ is the (configurational part of) the partition function of a system of $N+1$ interacting chain molecules and $Q(N, V, T) \times Q_{non-interacting}(1, V, T)$ the partition function for a system consisting of N interacting chains and one chain that does not interact with the others. The latter chain plays the role of the ideal gas molecule in the previous sections. Note, however, that although this molecule does not interact with any of the other molecules it *does* interact with itself, both through bonded and through non-bonded interactions. Unfortunately, this is not a particularly useful reference state, as we do not, in general, know the partition function of an isolated self-avoiding chain.

We therefore use another reference state, namely that of the isolated non-selfavoiding chain. To be specific, let us consider the case of a molecule that consists of ℓ segments. Starting from segment 1, we can add segment 2 in b_2 equivalent directions, and so on. Clearly, the total number of non-selfavoiding conformations is $\Omega_{id} = \prod_{i=1}^{\ell} b_i$. For convenience, I have assumed that for a given i , all b_i directions are equally likely (i.e. I ignore *gauche-trans* potential energy differences and I even allow the ideal chain to fold back on itself). These limitations are not essential but they simplify the notation. Finally, I assume that all b_i are the same. Hence, for the simple model that we consider, $\Omega_{id} = b^{\ell}$. If we use such an ideal chain as our reference system, the expression for the excess chemical potential becomes

$$\begin{aligned} \beta\mu_{ex} &= -k_B T \ln \left(\frac{Q_{chain}(N+1, V, T)}{Q(N, V, T)Q_{ideal}(1, V, T)} \right) \\ &= -k_B T \ln \langle \exp[-\beta\Delta U(\mathbf{q}^N, \mathbf{\Gamma}^N; \mathbf{q}_{N+1}, \mathbf{\Gamma}_{N+1})] \rangle, \end{aligned} \quad (34)$$

where ΔU denotes the interaction of the test chain with the N chains that are already present in the system *and with itself*, while $\langle \dots \rangle$ indicates averaging over all starting positions and all ideal-chain conformations of a randomly inserted chain.

The problem with the Widom approach to Eqn. 34 is that almost all randomly inserted ideal chain conformations will overlap either with particles already present in the system, or internally. The most important contributions to μ_{ex} will come from the extremely rare cases where the trial chain happens to be in just the right conformation to fit into the available space in the fluid. Clearly, it would be desirable if we could restrict our sampling to those conformations that satisfy this condition. If we do that, we introduce a bias in our computation of the insertion probability and we must somehow correct for that bias. In practice, the scheme involves two steps: in the first step a chain conformation is generated in such a way that 'acceptable' conformations are created with a high probability. The next step corrects for this bias by multiplying with a weight factor. A scheme that generates 'acceptable' chain conformations with a high probability

was developed by Rosenbluth and Rosenbluth in the early fifties [19]. In the Rosenbluth scheme, a conformation of a chain molecule is constructed segment-by-segment. For every segment, we have a choice of b possible directions. In the Rosenbluth scheme, this choice is not random but favors the direction with the largest Boltzmann factor. To be specific, the probability (P) to generate a polymer with a conformation Γ using the Rosenbluth algorithm is given by

$$P_{\Gamma} = \prod_{i=1}^{\ell} \frac{\exp[-\beta u^{(i)}(\Gamma_i)]}{Z_i}, \quad (35)$$

where $u^{(i)}(\Gamma_i)$ denotes the energy of segment i of the chain with conformation Γ (note that this energy excludes the contributions of segments $i+1$ to ℓ , so the total energy of the chain is given by: $U_{\Gamma} = \sum_{i=1}^{\ell} u^{(i)}(\Gamma_i)$). Z_i in equation 35 is shorthand for

$$Z_i \equiv \sum_{j=1}^b \exp[-\beta u^{(i)}(\Gamma_j)].$$

where j enumerates all possible orientations from which the i -th segment of the chain can be chosen and $u^{(i)}(\Gamma_j)$ denotes the potential energy of the i -th segment in orientation j . An important property of the probability given by Eqn. 35 is that it is normalized, i.e

$$\sum_{\Gamma} P_{\Gamma} = 1.$$

The Rosenbluth weight factor that corrects for the bias in the selection of conformation Γ is given by

$$W_{\Gamma} \equiv \prod_{i=1}^{\ell} \frac{Z_i}{b}. \quad (36)$$

Now let us assume that we use the Rosenbluth scheme to generate a large number of chain conformations while keeping the coordinates of all other particles in the system fixed. For this set of conformations, we compute the average of the Rosenbluth weight factor W , \overline{W} . If we also perform an ensemble average over all coordinates and conformations of the N particles in the system, we obtain

$$\langle W \rangle = \left\langle \sum_{\Gamma} P_{\Gamma}(\mathbf{q}^N, \Gamma^N) W_{\Gamma}(\mathbf{q}^N, \Gamma^N) \right\rangle, \quad (37)$$

where the angular brackets denote the ensemble average over all configurations of the system $\{\mathbf{q}^N, \Gamma^N\}$ of the 'solvent'. Note that the test polymer does not form part of the N -particle system. Therefore the probability to find the remaining particles in a configuration $\{\mathbf{q}^N, \Gamma^N\}$ does not depend on the conformation Γ of the polymer.

In order to simplify the expression for the average in Eqn. 37, we first consider the average of the Rosenbluth factor for a given configuration $\{\mathbf{q}^N, \Gamma^N\}$ of the solvent.

$$\overline{W}(\{\mathbf{q}^N, \Gamma^N\}) = \sum_{\Gamma} P_{\Gamma}(\mathbf{q}^N) W_{\Gamma}(\{\mathbf{q}^N, \Gamma^N\}) . \quad (38)$$

Substitution of equations (35) and (36) yields

$$\begin{aligned} \overline{W} &= \sum_{\Gamma} \left[\prod_{i=1}^{\ell} \frac{\exp[-\beta u^{(i)}(\Gamma_i)]}{Z_i} \right] \left[\prod_{i=1}^{\ell} \frac{Z_i}{b} \right] \\ &= \sum_{\Gamma} \prod_{i=1}^{\ell} \frac{1}{b} \exp[-\beta u^{(i)}(\Gamma_i)] \\ &= \sum_{\Gamma} \frac{1}{b^{\ell}} \exp[-\beta U_{\Gamma}] , \end{aligned} \quad (39)$$

where we have dropped all explicit reference to the solvent coordinates $\{\mathbf{q}^N, \Gamma^N\}$. Note that Eqn. 39 can be interpreted as an average over all *ideal* chain conformations of the Boltzmann factor $\exp[-\beta U_{\Gamma}]$. If we now substitute Eqn. 39 in Eqn. 38 we obtain

$$\langle W \rangle = \frac{\sum_{\Gamma} \langle \exp[-\beta \Delta U(\mathbf{q}^N, \Gamma^N; \mathbf{q}_{N+1}, \Gamma_{N+1})] \rangle}{\sum_{\Gamma} 1} . \quad (40)$$

If we compare Eqn. 40 with Eqn. 34, we see that the ensemble average of the Rosenbluth factor is directly related to the excess chemical potential of the chain molecule.

$$\beta \mu_{ex} = -k_B T \ln \langle W \rangle , \quad (41)$$

The above method to measure the chemical potential is not limited to chain molecules on a lattice. What *is* essential is that the number of possible directions for each segment (b) relative to the previous one is finite.

4.3. EXTENSION TO CONTINUOUSLY DEFORMABLE MOLECULES

The numerical computation of the (excess) chemical potential of a flexible chain (with or without elastic forces that counteract bending), is rather

different from the corresponding calculation for a chain molecule that has a large but fixed number of undeformable conformations. Below, I shall consider the case of a flexible molecule *with* internal energy. Consider a 'worm-like' chain of ℓ linear segments. The potential energy of a given conformation has two contributions:

1. The internal potential energy U_{int} is equal to the sum of the contributions of the individual joints. A joint between segments i and $i + 1$ (say) has a potential energy $u(\theta_i)$ that depends on the angle θ_i between the successive segments. For instance, $u(\theta_i)$ could be of the form $u(\theta) = \alpha\theta^2$. For realistic models for poly-atomic molecules, U_{int} would account for all local internal potential energy changes due to bending and torsion.
2. The 'external' potential energy U_{ext} . This energy accounts for all interactions with other molecules and for the non-bonded intra-molecular interactions. In addition, interactions with any external field that may be present are also included in U_{ext} .

In what follows I shall denote the chain in the absence of the 'external' interactions as the *ideal* chain. Clearly, the conformational partition function of the ideal chain is equal to

$$Z_{id} = c \int \cdots \int d\Gamma_1 \cdots d\Gamma_\ell \prod_{i=1}^{\ell} \exp(-\beta u_{id}(\theta_i)) \quad (42)$$

where c is a numerical constant. Our aim is to compute the effect of the external interactions on the conformational partition function. Hence, we wish to evaluate Z/Z_{id} , where Z denotes the partition function of the interacting chain. The excess chemical potential of the interacting chain is given by

$$\mu_{ex} = -k_B T \ln(Z/Z_{id}).$$

The numerical procedure to compute the chemical potential is similar to the scheme to compute the excess chemical potential of a chain molecule with fixed conformations 4.2. Yet, there is an important difference precisely because the number of conformations is now, in principle, infinite. We can never hope to sample over *all* possible orientations of a new segment as we grow a chain. Hence, we generate a random sample of possible segment directions and use these in a modified Rosenbluth scheme. To compute μ_{ex} , we apply the following 'recipe' to construct a conformation of a chain of ℓ segments. The construction of chain conformations proceeds segment by segment. Let us consider the addition of one such segment. To be specific, let us assume that we have already grown i segments, and that we are trying to add segment $i + 1$. This is done as follows:

1. Generate a fixed number (say b) trial segments. The orientations of the trial segments are distributed according to the Boltzmann weight associated with the internal energy $u(\theta)$. We denote the different trial segment by indices $1, 2, \dots, b$.
2. For all b trial segments, we compute the 'external' Boltzmann factor $\exp(-\beta u_{ext}(j))$.
3. Select one of the trial segments, say j , with a probability

$$P_j = \frac{\exp(-\beta u_{ext}(j))}{Z_i},$$

where we have defined

$$Z_i \equiv \sum_{j'=1}^b \exp(-\beta u_{ext}(j')).$$

4. Add this segment as segment $i + 1$ to the chain and store the corresponding partial Rosenbluth weight $w_i = Z_i/b$.

The desired ratio Z/Z_{id} is then equal to the average value (over many trial chains) of the product of the partial Rosenbluth weights:

$$Z/Z_{id} = \langle \prod_{i=1}^{\ell} w_i \rangle. \quad (43)$$

The advantage of this scheme is that step 3 biases the sampling towards energetically favorable conformations. However, it still remains to be shown that equation 43 is, in fact, correct. To show this, we consider the probability to generate a given chain conformation. This probability is the product of a number of factors. Let us first consider these factors for one segment, and then later extend the result to the complete chain. The probability to generate a given set of b trial segments with orientations Γ_1 through Γ_b is

$$P_{id}(\Gamma_1) \cdot P_{id}(\Gamma_2) \cdots P_{id}(\Gamma_b) d\Gamma_1 \cdots d\Gamma_b.$$

The probability of selecting any one of these trial segments, say segment j , is

$$\frac{\exp(-\beta u_{ext}(j))}{Z_i}.$$

We wish to compute the average of a quantity, say w , over all possible sets of trial segments and all possible choices of the segment. To this end, we must sum over all j and integrate over all orientations $\prod_{j'=1}^b d\Gamma_{j'}$ (i.e. we

We wish to compute the average of a quantity, say w , over all possible sets of trial segments and all possible choices of the segment. To this end, we must sum over all j and integrate over all orientations $\prod_{j'=1}^b d\Gamma_{j'}$ (i.e, we average over the normalized probability distribution for the orientation of segment $i + 1$):

$$\langle w \rangle = \int \left[\prod_{j'=1}^b d\Gamma_{j'} P_{id}(\Gamma_{j'}) \right] \sum_{j''=1}^b \frac{\exp(-\beta u_{ext}(j''))}{Z_i} w(1, 2, \dots, b). \quad (44)$$

Now we make use of the fact that $w_i(1, 2, \dots, b)$ is equal to Z_i/b (see step 4 of the 'recipe' above). Inserting this expression in Eqn. 44, we obtain:

$$\langle w \rangle = \int \left[\prod_{j'=1}^b d\Gamma_{j'} P_{id}(\Gamma_{j'}) \right] \sum_{j''=1}^b \frac{\exp(-\beta u_{ext}(j''))}{b}. \quad (45)$$

As the labeling of the trial segments is arbitrary, all b terms in the sum in Eqn. 45 yield the same contribution, and Eqn. 45 simplifies to

$$\langle w \rangle = \int d\Gamma P_{id}(\Gamma) \exp(-\beta u_{ext}(\Gamma)) \quad (46)$$

$$= \frac{\int d\Gamma \exp(-\beta[u_{id}(\Gamma) + u_{ext}(\Gamma)])}{\int d\Gamma \exp(-\beta u_{id}(\Gamma))} \quad (47)$$

$$= \frac{Z^{(1)}}{Z_{id}^{(1)}}, \quad (48)$$

which is indeed the desired result, but for the fact that the expression in Eqn. 46 refers to one segment (as indicated by the superscript in $Z^{(1)}$). The extension to a chain of ℓ segments is straightforward, be it that the intermediate expressions become a little unwieldy.

5. Configurational bias Monte Carlo scheme

Up to this point, I have been speaking about techniques to estimate the chemical potential of flexible molecules. However, the Rosenbluth trial insertion scheme can be used as a starting point for a Monte Carlo scheme to sample equilibrium configurations of systems consisting of chain molecules. At first sight, this may not appear to be a new result but a very old one. After all, the original Rosenbluth scheme itself was designed as a method to sample polymer conformations. However, the Rosenbluth scheme suffers from the drawback that it generates an unrepresentative sample of all polymer conformations: i.e. the probability to generate a particular conformation Γ using the Rosenbluth scheme, is *not* proportional to the Boltzmann weight of that conformation. The Rosenbluth weight W , discussed in

works for relatively short chains. This drawback of the Rosenbluth sampling scheme is, in fact, well known (see, e.g. [20]). The solution of this problem is to bias the Rosenbluth sampling in such a way that the correct (Boltzmann) distribution of chain conformations is generated in a Monte Carlo sequence. In the configurational bias scheme, the Rosenbluth weight is used to bias the *acceptance* of trial conformations that are generated with the Rosenbluth procedure. As a consequence, all conformations are generated with their correct Boltzmann weight. This removes the main drawback of the original Rosenbluth scheme. For details, I refer the reader to ref. [21].

The CBMC scheme has been applied to several models for lyotropic liquid crystals. Dijkstra and Frenkel studied the effect of flexibility on the I-N transition of semi-flexible hard rods [22] and subsequently, Polson and Frenkel combined the scaling approach described above with CBMC to study the effect of flexibility on the N-Sm transition [23].

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