

# Order through disorder: Entropy-driven phase transitions.

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## 1 Introduction

In this lecture, I wish to discuss the role of entropy in phase transitions. At first sight, there is little need for such a discussion. The second law of thermodynamics tells us that, in a closed system at equilibrium, the entropy,  $S$ , is at a maximum. One could therefore argue that any spontaneous phase transformation in a closed system occurs simply because it results in an increase of the entropy. However, it is more common to consider the equilibrium behavior of a system that is not isolated, but can exchange energy with its surroundings. In that case, the second law of thermodynamics implies that the system will tend to minimize its Helmholtz free energy  $F = E - TS$ , where  $E$  is the internal energy of the system and  $T$  the temperature. Clearly, a system at constant temperature can lower its free energy in two ways: either by *increasing* the entropy  $S$ , or by *decreasing* the internal energy  $E$ . In order to gain a better understanding of the factors that influence phase transitions, we must look at the statistical mechanical expressions for entropy. The simplest starting point is to use Boltzmann's expression for the entropy of an isolated system of  $N$  particles in volume  $V$  at an energy  $E$ ,

$$S = k_B \ln \Omega \quad (1)$$

where  $k_B$ , the Boltzmann constant, is simply a constant of proportionality.  $\Omega$  is the total number of (quantum) states that is accessible to the system. In the remainder of this paper, I shall choose my units such that  $k_B=1$ . The usual interpretation of eqn. 1 is that  $\Omega$ , the number of accessible states of a system, is a measure for the "disorder" in that system. The larger the disorder, the larger the entropy. This interpretation of entropy suggests that a phase transition from a disordered to a more ordered phase can only take place if the loss in entropy is compensated by the decrease in internal energy. This statement is completely correct, provided that we use eqn. 1 to *define* the amount of disorder in a system. However, we also have an *intuitive* idea of order and disorder: crystalline solids are "ordered", while isotropic liquids are "disordered". This suggests that a spontaneous phase transition from the fluid to the crystalline state can only take place if the freezing lowers the internal energy of the system sufficiently to outweigh the loss in entropy: i.e. the ordering transition is "energy driven". In many cases, this is precisely what happens. It would, however, be a mistake to assume that our intuitive definition of order always coincides with

the one based on eqn. 1. In fact, the aim of this paper is precisely to show that many "ordering"-transitions that are usually considered to be energy-driven may, in fact, be entropy driven. At the outset, I should stress that the idea of entropy-driven phase transitions is an old one. However, it has only become clear during the past few years that such phase transformations may not be interesting exceptions, but the rule!

The question that I wish to address is therefore: what classes of phase transitions can be driven by entropy alone? In order to answer this question, we must consider systems in which the internal energy is a function of temperature alone. If a first-order phase transformation takes place at a constant temperature, the internal energy must remain the same. Hence the change in Helmholtz free energy is determined exclusively by the change in entropy of the system. In general, it is not obvious how to devise model systems for which the internal energy depends only on temperature. In order for this condition to hold, the partition function  $Z$  of the system should factorize into a part that depends only on the temperature,  $T$ , and a part that depends on the density,  $\rho$ . For a *classical*  $N$ -body system, we can write  $Z$  as

$$Z = \frac{1}{h^{3N} N!} \int \cdots \int d\mathbf{p}^N d\mathbf{q}^N \exp[-\beta H(\mathbf{p}^N, \mathbf{q}^N)], \quad (2)$$

where  $\beta = (k_B T)^{-1}$ , while  $H(\mathbf{p}^N, \mathbf{q}^N)$  denotes the Hamiltonian of the system, expressed as a function of the momenta  $\mathbf{p}^N$  and the coordinates  $\mathbf{q}^N$ . For convenience, I have assumed that we are dealing with an atomic system. The Hamiltonian  $H$  is the sum of the kinetic energy  $K(\mathbf{p}^N)$  and the potential energy  $U(\mathbf{q}^N)$ . For classical systems, we can perform the integration over momenta in eqn. 2 analytically. It yields a factor in the partition function that depends on  $T$  only. The remaining, configurational, part of the partition function is:

$$Q = \frac{1}{N!} \int \cdots \int d\mathbf{q}^N \exp[-\beta U(\mathbf{q}^N)]. \quad (3)$$

In general,  $Q$  will be a function of  $N, V$  and  $T$ . We are interested in the case that  $Q$  does not depend on  $T$ . It would seem that this is not possible, because  $Q$  depends on  $\beta$ . However, if we limit our attention to *hard-core* potentials, *i.e.* potential energy functions that are (depending on the value of  $\mathbf{q}^N$ ) either 0 or  $\infty$ , then  $Q$  is indeed independent of  $\beta$ . It is easy to see that, in that case, the average potential energy of the system

$$\langle U \rangle \equiv -\frac{\partial \ln Q}{\partial \beta} = 0. \quad (4)$$

The average energy of a hard-core system is therefore simply equal to the average kinetic energy  $\langle K \rangle$ , which is a function of the temperature only. As the internal energy of a hard-core system is constant at constant temperature, any phase transformation in such a system takes place only because this results in an increase in entropy.

Now that we have defined a class of model systems for which entropy is the *only* driving force behind spontaneous phase transformations, we wish to find out what kinds of phase such a model system can exhibit.

## 2 (Liquid) Crystals

In this section, I shall briefly review what we now know about the effect of entropy on the formation of partially ordered liquids ("liquid crystals") and crystalline solids. The earliest example of an entropy-driven ordering transition is described in a classic paper of Onsager [1], on the isotropic-nematic transition in a (three-dimensional) system of thin hard rods. Onsager showed that, on compression, a fluid of thin hard rods of length  $L$  and diameter  $D$  *must* undergo a transition from the isotropic fluid phase, where the molecules are translationally and orientationally disordered, to the nematic phase. In the latter phase, the molecules are translationally disordered, but their orientations are, on average, aligned. This transition takes place at a density such that  $(N/V)L^2D = \mathcal{O}(1)$ . Onsager considered the limit  $L/D \rightarrow \infty$ . In this case, the phase transition of the hard-rod model can be found exactly (see e.g. ref. [2]). At first sight it may seem strange that the hard rod system can *increase* its entropy by going from a disordered fluid phase to an orientationally ordered phase. Indeed, due to the orientational ordering of the system, the orientational entropy of the system decreases. However, this loss in entropy is more than offset by the increase in translational entropy of the system: the available space for any one rod increases as the rods become more aligned. In fact, we shall see this mechanism returning time-and-again in ordering transitions of hard-core systems: the entropy *decreases* because the density is no longer uniform in orientation or position, but the entropy *increases* because the free-volume per particle is larger in the ordered than in the disordered phase.

The most famous, and for a long time controversial, example of an entropy-driven ordering transition is the freezing transition in a system of hard spheres. This transition had been predicted by Kirkwood in the early fifties [3] on basis of an approximate theoretical description of the hard-sphere model. As this prediction was quite counter-intuitive and not based on any rigorous theoretical results, it met with wide-spread skepticism until Alder and Wainwright [4] and Wood and Jacobson [5] performed numerical simulations of the hard-sphere system that showed direct evidence for this freezing transition. Even then, the acceptance of the idea that freezing could be an *entropy* driven transition, came only slowly [6]. However, by now, the idea that hard spheres undergo a first-order freezing transition is generally accepted. And, although the hard-sphere model was originally devised as an idealized and highly unrealistic model of an atomic fluid, it is now realized that this model provides a good description of certain classes of colloidal systems (see the lectures by Lekkerkerker [7]).

The next step in this sequence came in the mid-eighties when computer simulations [8] showed that hard-core interactions alone could also explain the formation of more complex liquid crystals. In particular, it was found that a sys-

tem of hard spherocylinders (i.e. cylinders with hemi-spherical caps) can form a smectic liquid crystal, in addition to the isotropic liquid, the nematic phase and the crystalline solid. In the smectic (A) phase, the molecules are orientationally ordered but, in addition, the translational symmetry is broken: the system exhibits a one-dimensional density-modulation. Subsequently, it was found that some hard-core models could also exhibit columnar ordering [9]. In the latter case, the molecules assemble in liquid-like stacks, but these stacks order to form a two-dimensional crystal. In summary, hard-core interaction can induce orientational ordering and one-, two- and three-dimensional positional ordering. This is rather surprising because, in particular for the smectic and the columnar phase, it was generally believed that their formation required specific energetic interactions.

After reading the above "history" of entropic phase-transitions, the reader may wonder if there is, in fact, *any* class of phase transitions for which energy must be invoked as the driving force. The answer is undoubtedly yes: magnetic phase transitions are typical "energy driven" transitions, as is the liquid-vapor transition. However, there are certainly more entropy driven transitions than the ones listed above. In the next section, I shall discuss a surprisingly simple example.

### 3 Binary mixtures

Phase separation in binary mixtures is the example that is used in many textbooks to illustrate the competition between energy and entropy in a phase transformation. For a mixture at constant total volume  $V$ , the Helmholtz free energy  $F$ , should be minimal. As a first approximation, the entropy of mixing of a mixture of two species  $A$  and  $B$ , is replaced by the entropy of mixing of an ideal mixture

$$S_{id}(X) = -Nk_B[X \ln X + (1 - X) \ln(1 - X)] \quad (5)$$

where  $X$  denotes the mole-fraction of one component (say  $A$ ):  $X = N_A/(N_A + N_B)$ . The entropy of mixing given by eqn. 5 is a convex function of  $X$ . As a consequence,  $S_{id}(X)$  will always decrease if phase separation takes place. This implies that phase separation can only take place if the resulting decrease in energy  $E$  outweighs the increase in  $-TS_{id}$ . In a hard-core mixture, there is no energy change upon mixing. Hence, if eqn. 5 were exact, we should never observe phase separation in a hard-core mixture. And, even though eqn. 5 is known to be only an approximation, it was commonly thought that a fluid mixture of dissimilar hard spheres would not phase separate. This belief was, at least partly, based on the work of Lebowitz and Rowlinson [10], who studied the phase-behavior of such binary mixtures of dissimilar hard spheres, using a more accurate approximation for the entropy of mixing, based on the Percus-Yevick (PY) integral equation. Lebowitz and Rowlinson found that, at least within that approximation, hard spheres of arbitrary size ratio will mix in all proportions in the fluid phase. The implication of this result was that entropic effects are not enough to cause a miscibility gap in a simple fluid mixture. Recently, however, Biben

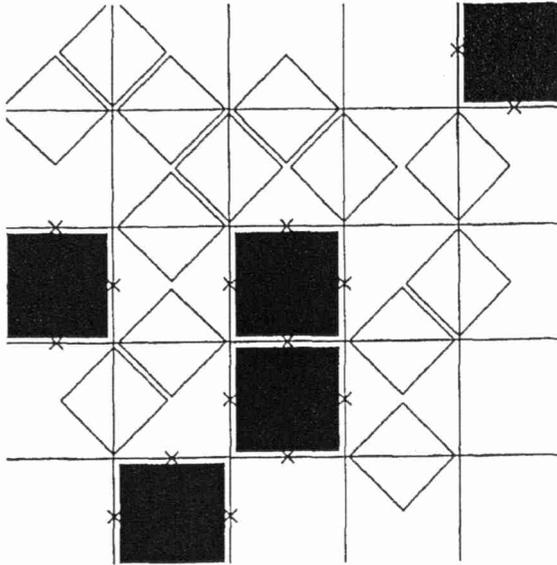


Fig. 1. Exactly solvable lattice-gas model for a mixture of large (black squares) and small (white squares) hard particles. The crosses indicate which small-particle sites are excluded by the presence of large particles.

and Hansen [11] have applied a more sophisticated analytical theory for dense fluid mixtures to the same problem. Unlike the PY approximation, this theory is found to predict that an asymmetric binary hard-sphere mixture should phase separate if the sizes of the two spheres are sufficiently dissimilar (typically, if the size ratio is less than 0.2). However, as in the case of ref. [10], it is based on an approximate theory for the hard-sphere mixture. Hence, one may wonder to what extent the result found in ref. [11] depends on the approximations that are used to compute the equation-of-state of the mixture. Clearly, it would be highly desirable to have a model system of a binary mixture for which the existence of a purely entropic demixing transition can be proven exactly.

It turns out that, in a special case [12], this can indeed be done by constructing a simple lattice model of binary hard-core mixture. By transforming to a grand-canonical ensemble, this binary hard-core mixture can be mapped onto one-component lattice gas with attractive nearest neighbor interactions. This mapping is of interest because the one-component lattice gases can, in turn, be mapped onto Ising-like models for which, in some cases, the phase behavior is known exactly. To illustrate our approach, first consider a trivial model-system, namely a square lattice with at most one particle allowed per square. Apart from the fact that no two particles can occupy the same square face, there is no interaction between the particles. For a lattice of  $N$  sites, the grand-canonical partition function is:

$$\mathcal{E} = \sum_{\{n_i\}} \exp[\beta\mu \sum_i n_i] \quad (6)$$

The sum is over all allowed sets of occupation numbers  $\{n_i\}$  and  $\mu$  is the chemical potential. Next, we include “small” hard particles that are allowed to sit on the links of the lattice. (see Fig. 1). These small particles are excluded from the edges of a square that is occupied by a large particle.

For a given configuration  $\{n_i\}$  of the large particles, one can then exactly calculate the grand canonical partition function of the small particles. Let  $M = M(\{n_i\})$  be the number of free spaces accessible to the small particles. Then clearly:

$$\mathcal{E}_{small}(\{n_i\}) = \sum_{l=0}^M \frac{M! z_s^l}{l!(M-l)!} = (1+z_s)^{M(\{n_i\})}, \quad (7)$$

where  $z_s$  is the fugacity of the small particles.  $M$  can be written as

$$M(\{n_i\}) = 2N - 4 \sum_i n_i + \sum_{\langle ij \rangle} n_i n_j, \quad (8)$$

where  $2N$  is the the number of links on the lattice and the second sum is over nearest-neighbor pairs and comes from the fact that when two large particles touch, one link is doubly excluded [13]. the total partition function for the “mixture” is:

$$\mathcal{E}_{mixture} = \sum_{\{n_i\}} \exp[(\beta\mu - 4 \log(1+z_s)) \sum_i n_i + [\log(1+z_s)] \sum_{\langle ij \rangle} n_i n_j], \quad (9)$$

where we have omitted a constant factor  $(1+z_s)^{2N}$ . Eqn. 9 is simply the expression for the grand-canonical partition function of a one-component lattice-gas Ising model with a shifted chemical potential and an effective nearest neighbor attraction with an interaction strength  $\log(1+z_s)/\beta$ . As is well known, this lattice model can again be transformed to a 2-D Ising spin model that can be solved in the zero field case [14, 15]. In the language of our mixture model, no external magnetic field means:

$$(1+z_s)^2 = z_l, \quad (10)$$

where  $z_l = \exp \beta\mu$ , the large particle fugacity. The order-disorder transition in the Ising model then corresponds to phase separation in the language of our model. This de-mixing is purely entropic, just like the transition predicted by [11] for the hard sphere mixture. In fact, the mapping described above can also be carried through when energetic interactions between the large particles are included. However, for the sake of clarity, we will restrict ourselves to athermal hard-core mixtures.

Of course, there is a wide variety of lattice models for hard-core mixtures that can be mapped onto one-component systems with effective attraction. The model discussed above is only special in the sense that it can be mapped onto a model that is exactly solvable. In particular, from the known results for the 2D-

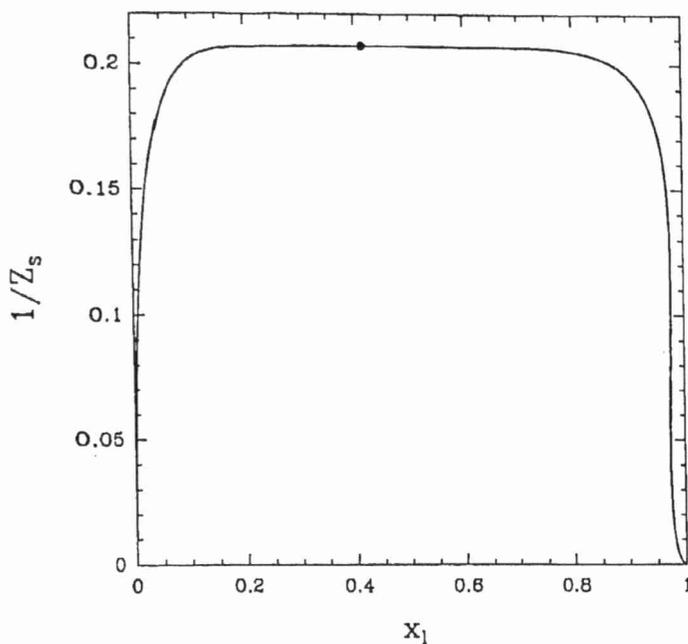


Fig. 2. Phase diagram of the model system shown in figure 1.  $X_l$  denotes the molar fraction of large squares,  $z$ , is the fugacity of small squares. The drawn curve indicates the composition of coexisting phases. Note that this curve is asymmetric. In particular, the critical point (indicated by a black dot) is located at  $X_l = 2^{\frac{1}{2}} - 1$ . Along the coexistence curve the fugacities of the large and small particles are related through equation 10)).

Ising model (see e.g. [16]), it is straightforward to evaluate the composition of the coexisting phases along the entire coexistence line. This coexistence curve is shown in Fig. 2. One important question that is raised by the work of Biben and Hansen [11] is whether the de-mixing transition is of the fluid-fluid or the fluid-solid type. The phase transition in the square-lattice model that we discussed above provides no answer to this question, as there is no distinction between "liquid" and "solid" in a lattice-gas on a square, or simple-cubic lattice. Yet, from the above mapping, it is immediately obvious that a fluid-fluid transition does, in fact, occur in another hard-core mixture, namely that of a mixture of hard-core monomers and polymers on a lattice. To this end, we consider, once again our model of a mixture of large and small hard squares (cubes, in 3D) on a square (cubic) lattice, i.e. the model that could be mapped onto the 1-component lattice gas with nearest neighbor interactions. We now construct "polymers" by connecting  $N$  large squares (cubes), while the solvent is represented by the small particles. The simplest polymers are made by connecting  $N$  large particles by nearest neighbor bonds only. A grand-canonical summation over all configurations of the small particles, yields a very simple expression for the (canonical) partition function of the polymers, namely

$$Z_{polymers} = \sum_{\{n_i\}} \exp\left[\frac{J}{k_B T} \sum_{\langle ij \rangle} n_i n_j\right] \quad (11)$$

with  $J \equiv k_B T \log(1 + z_s)$  and where the sum is over all acceptable (i.e. non-overlapping) configurations of the hard-core polymers. Eqn. 11 is precisely the expression for the partition function of the Flory-Huggins lattice model [17]. This model has been studied extensively both using approximate analytical theories, in particular the well-known Flory-Huggins theory and modifications thereof (for a critical review see [18]) and, more recently, by direct numerical simulations (see e.g. [19, 20]). Traditionally, the coupling constant  $J$  has been interpreted as a purely *energetic* interaction. In contrast, in the context of the model that we consider,  $J$  is of completely entropic origin. We can now translate the results that have been obtained for the Flory-Huggins lattice-gas model directly to our hard-core mixture. This means that many effects that in the past were interpreted as originating from energetic attractions, can also be obtained from purely entropic effects. In particular, the existence of a first-order fluid-fluid phase separation in this model provides direct proof that a purely entropic de-mixing transition exists in a hard-core polymer-solvent mixture. Our analysis also yields a very simple ‘entropic’ interpretation of other, closely related phenomena, such as polymer collapse in a ‘poor’ solvent. It is, perhaps, worth pointing out that in our model, the solvent molecules are smaller than the monomeric units of the polymer. In contrast, in the original Flory-Huggins lattice model, there is no such size-asymmetry. We can, however, construct a hard-core lattice model where solvent and monomeric units occupy the same volume. It can be shown that the solvent-induced polymer collapse will also occur in such a ‘symmetric’ model system.

Finally, we note that the Flory-Huggins theory for polymer solutions yields the following (approximate) expression for the free-energy a polymer solution:

$$\frac{F_{mix}}{k_B T} = \frac{\phi}{N} \log \phi + (1 - \phi) \log(1 - \phi) + \chi \phi(1 - \phi) \quad (12)$$

where  $\phi$  is the fraction of the volume occupied by polymer, while the parameter  $\chi$  is related to the coupling constant  $J$  of the original lattice model, by

$$\chi = \frac{1}{2} \frac{J}{k_B T} n_b = \frac{1}{2} n_b \ln(1 + z_s), \quad (13)$$

where  $n_b$  is the coordination number of the lattice. If, as was assumed in the original Flory-Huggins theory,  $J$  is due to energetic interactions, then  $\chi$  should vary as  $1/T$ . However, in the present (extreme) interpretation of the same lattice-gas model, the parameter  $\chi$  would be *completely independent of temperature*. There is, in fact, a large body of experimental data that shows that, for many polymer solutions,  $\chi$  has a large, if not dominant, entropic (i.e. temperature-independent) part.

## 4 Depletion Flocculation

Let us next consider a slightly more complex example of an entropy-driven phase separation in a binary mixture, namely polymer-induced flocculation of colloids. Experimentally, it is well known that the addition of a small amount of free, non-adsorbing polymer to a colloidal suspension induces an effective attraction between the colloidal particles and may even lead to coagulation. This effect has been studied extensively [21] and is well understood, at least qualitatively. As in the example discussed above, the polymer-induced attraction between colloids is an *entropic* effect: when the colloidal particles are close together, the total number of accessible polymer conformations is larger than when the colloidal particles are far apart. However, although the physical mechanism responsible for polymer-induced coagulation is understood *qualitatively*, a quantitative description of this phenomenon is difficult. This is so because the polymer-induced attraction between the colloidal particles is non-pairwise additive. Moreover, it depends both on the osmotic pressure of the polymer and on the concentration of the colloid. Yet, in the theoretical description of polymer-induced clustering [22], the effect of the polymer is usually replaced by an effective, density-independent, pair-wise additive attraction between the colloidal particles. However, in this case, no analytical evaluation of the (grand-canonical) partition function is possible, even when one considers only the very simplest model, *viz.* that of a mixture of hard-core colloidal particles with ideal chain molecules with conformations that are restricted to a lattice. In this case, it would clearly be desirable to carry out ‘exact’ numerical simulations to investigate the phase behavior. Yet, the computational problems are still formidable. What is required is a numerical scheme that samples the positions of the colloidal particles while averaging over all possible conformations of a large (and fluctuating) number of chain molecules. The ‘conventional’ Monte Carlo schemes to simulate lattice models of polymer systems [20] would be woefully inadequate for such a calculation.

Fortunately, it is possible to construct a rigorous and efficient Monte Carlo scheme to study this model. Our approach relies on the fact that we can recursively compute the partition function of an ideal (non-self avoiding) chain on a lattice in an arbitrary external potential [23, 24]. This is most easily seen by considering a chain of length  $\ell - 1$  on a lattice. For convenience, we assume that the external potential is either zero or infinite. The total number of accessible ideal chain conformations that terminate on lattice site  $i$  is denoted by  $\omega_{\ell-1}(i)$ . The total partition function  $\Omega_{\ell-1}$  is equal to  $\sum_i \omega_{\ell-1}(i)$ , where the sum runs over all lattice sites. The total number of chains of length  $\ell$  that terminate on site  $i$  is clearly equal to the sum of the total number of chains of length  $\ell - 1$  that terminate on any of the neighbors of  $i$ , multiplied by the Boltzmann factor associated with site  $i$ . Using such a recursive scheme, we can compute *exactly*  $\Omega_\ell$ , the partition function of a single ideal polymer of arbitrary length  $\ell$  on a lattice, in an arbitrary external potential. This scheme can be used as a starting point to study self-avoiding polymers [25, 26], but for the present purpose we limit ourselves to ideal polymers. Up to this point we have not specified the

nature of the 'external' potential. We now assume that this potential is due to the presence of  $N$  hard, spherical colloidal particles each of which occupies many lattice sites. The polymer partition function clearly depends on the coordinates  $\mathbf{r}^N$  of the colloidal particles:  $\Omega_\ell(\mathbf{r}^N)$ . The configurational part of the partition function of the system of  $N$  colloids plus one polymer of length  $\ell$  in volume  $V$  is then given by:

$$Z(V, N, 1) = \int_V d\mathbf{r}^N e^{-U_{hs}(\mathbf{r}^N)} (\Omega_\ell(\mathbf{r}^N)), \quad (14)$$

where  $U_{hs}(\mathbf{r}^N)$  denotes the hard-sphere interaction. Next, we make use of the fact that we are considering *ideal* polymers. In that case we can immediately write down the corresponding partition function for  $N$  colloids and  $M$  ideal polymers:

$$Z(V, N, M) = \int_V d\mathbf{r}^N e^{-U_{hs}(\mathbf{r}^N)} (\Omega_\ell(\mathbf{r}^N))^M / M!, \quad (15)$$

where the factor  $1/M!$  accounts for the fact that the polymers are indistinguishable. Using eq. 15 it is straightforward to transform to an ensemble where the polymer chemical potential (i.e. the osmotic pressure) is kept fixed. The corresponding grand-canonical partition function is given by:

$$\begin{aligned} \Xi(V, N, \mu) &= \sum_{M=0}^{\infty} e^{M\mu_{ch}} Z(V, N, M) / M! \\ &= \int_V d\mathbf{r}^N e^{-U_{hs}(\mathbf{r}^N)} \sum_{M=0}^{\infty} e^{M\mu_{ch}} (\Omega_\ell(\mathbf{r}^N))^M / M! \\ &= \int_V d\mathbf{r}^N e^{-U_{hs}(\mathbf{r}^N)} e^{z\Omega_\ell(\mathbf{r}^N)}. \end{aligned} \quad (16)$$

In the last line of eq. 16, we have introduced the polymer fugacity  $z \equiv e^{\mu_{ch}}$ , where  $\mu_{ch}$  denotes the chemical potential of the chain molecules.

The important point to note is that eq. 16 allows us to evaluate the properties of the colloidal particles in osmotic equilibrium with a polymer reservoir. In particular, it shows that we can perform Monte Carlo sampling of the colloidal particles. The polymers only affect  $U_{eff}(\mathbf{r}^N)$ , the effective interaction between the colloidal particles:

$$U_{eff}(\mathbf{r}^N) \equiv U_{hs}(\mathbf{r}^N) - z \Omega_\ell(\mathbf{r}^N). \quad (17)$$

$z\Omega_\ell(\mathbf{r}^N)$  measures the entropic interaction between the colloids due to *all* possible polymer conformations. This entropic interaction is, in principle, not pairwise additive. In fact, it is shown in ref. [24], that for all but the shortest chain molecules, this non-additivity of the polymer-induced interaction between the colloids, has a pronounced effect on the structure and stability of the mixture. For more details, we refer the reader to ref. [24].

## 5 From Soap to Saturn?

Finally, I wish to discuss a more speculative, and somewhat exotic, example of an entropy-driven phase transition, namely the demixing of a system of ideal point fermions (“non-interacting electrons”) and classical fluid particles. The analogy between this system and the previous ones rests on the fact that, in Feynman’s path-integral formulation of quantum mechanics, there is an isomorphism between the partition-function of a  $d$ -dimensional quantum-mechanical system, and that of a  $d + 1$ -dimensional, “polymer” system. Ideal quantum particles in  $d$  dimensions can be described by ideal, directed polymers in  $d + 1$  dimensions. This suggests that we may expect that mixtures of ideal quantum particles and atoms (effectively, hard spheres) behave much like a mixture of ideal polymers and colloids. In fact, the situation in the quantum case is complicated by the fact that one must take exchange into account. This is relatively straightforward in the case of numerical simulations of bosons [28], but it creates serious problems for fermions (the ‘sign’-problem). However, in ref. [29], it is shown how, at least for a mixture of atoms and ideal fermions, these problems may be overcome. Alavi and Frenkel [29] show that it is, in fact, possible to evaluate numerically (but exactly) the grand-canonical partition function of ideal fermions in the presence of arbitrary “obstacles” (in particular, atoms). This makes it possible to perform Monte Carlo sampling of the atomic positions in the presence of the fermion ‘bath’. Here, I will not discuss the technical aspects of these simulations. Rather, I will summarize the main conclusion, which is that there is indeed strong evidence for a demixing transition as the chemical potential of the fermions is increased beyond a certain critical value. Again, there are no attractive forces in this system. Hence, this fermion-induced phase separation appears to be yet another example of “attraction through repulsion”. For more details, the reader is referred to ref. [29]. It is amusing to note that the phase-separation in a mixture of ideal fermions and hard-spherical “atoms” may have an intriguing counterpart in planetary astronomy, namely in the structure of the interior of Saturn. It is thought that the core of Saturn, which is a hydrogen-helium planet, consists of nearly pure helium [30], whilst at the conditions relevant to the interior of Saturn ( $T \approx 10^4\text{K}$ ,  $P \approx 1 - 10\text{Mbar}$ ) the hydrogen probably is metallic. If we view the helium as consisting of ‘hard-spheres’, and the metallic hydrogen as a nearly free electron gas (in which the hydrogen nuclei play the role of a neutralising background), we might expect on the basis of the calculations in ref. [29] that such a mixture would phase-separate. Clearly, this example is far removed from “complex” liquids, but it does provide a nice illustration of the unity of physics.

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