Combinatorial Entropy and the Statistical Mechanics of Polydispersity

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A new method to treat statistical mechanics in a polydisperse system is described, applicable when the nonideal part of the free energy depends only on a few moments of a size distribution. A simple entropic contribution to the free energy is identified from combinatorial considerations. Although approximate in the general case, the method obtains the exact spinodal curve, critical points, cloud curve, and shadow curve. Polydisperse Flory-Huggins theory is treated as an example. [S0031-9007(97)05161-2]

Crude oil, polymers, commercial surfactants, and colloidal suspensions are typical examples of industrially important polydisperse systems. The thermodynamics and phase behavior of such systems underly, at least in part, important processing characteristics, storage stability, and other properties. Thermodynamically, a polydisperse system can be regarded as a system with a continuously infinite species type [1–4]. In some cases (colloids), it genuinely is the case that every particle is (subtly) different from every other. In other cases (crude oil, polymers), the number of species is large but finite (10^2–10^5, say).

Subtleties, too, arise in the representation of the phase behavior of polydisperse systems. Instead of a binodal region with tie lines, for instance, one should think of a *cloud curve* giving the compositions at which phase separation just starts to occur, and a *shadow curve* giving the composition of the newly emerging phase [1].

Frequently, the excess free energy of a polydisperse system depends only on a few moments of a size distribution. Examples include polydisperse Flory-Huggins theory [2], the polydisperse hard sphere fluid [3], and polydisperse hard rods in 1D [4]. In this Letter, I discuss a novel and general analysis which reduces the overall thermodynamic description to an equivalent finite component problem involving moment variables. The use of moment variables has been considered previously by Irvine and Gordon [5], and Beerbaum *et al.* [6], but only to derive truncation theorems for the spinodal and critical point conditions. Their results can be derived from the present theory as a special case.

To focus the discussion, consider a system of N particles in a volume V, at a density $\rho = N/V$. Suppose that each particle has a property σ_i (particle diameter or chain length, for instance), drawn from some distribution $p(\sigma)$. If the system is monodisperse all of the particles have the same σ_i, in which case i is just a passive label. In general, there may be any number of different species, or all particles may be genuinely different. The moment variables referred to above are quantities such as $m_n = \sum_{i=1}^{N} f_n(\sigma_i)/N$, where the $f_n(\sigma)$ are various functions of σ. The idea is to use the quantities ρm_n

as thermodynamic density variables [this includes ρ as a special case, when $f_n(\sigma) = 1$]. For instance, if phase separation occurs, tie lines in (ρm_n) space are straight, and the lever rule applies.

Even if the excess free energy depends only on the moment variables, the ideal part still depends explicitly on the distribution $p(\sigma)$ through the entropy of the mixing term. This prevents an immediate transformation to moment variables. As is well known, entropy of mixing comes from the factor $1/N!$ in the partition function, or $1/\prod_i N_i!$ for a multicomponent system. This in turn is usually derived from the classical limit of quantum statistics [7], but a rigorous derivation in classical statistical mechanics is both possible, and necessary to identify the corresponding term in the moment description.

To do this, follow Gibbs [8] and define a (nonextensive) free energy F' via

$$e^{-\beta F'} = \int d\Gamma \, e^{-\beta H(\Gamma)}, \quad (1)$$

where $\beta = 1/k_B T$ is inverse temperature (k_B is the Boltzmann's constant), H is the Hamiltonian, and the integral is over all phase space configurations Γ. No $1/N!$ appears in this, as all particles are distinguishable. This factor reappears though when computing the free energy of two or more systems considered together. Suppose that two systems containing N_1 and N_2 particles are considered as a joint system. Following the prescription in Eq. (1), the free energy of the joint system is found from

$$e^{-\beta F'} = \sum_{\text{prtns}} e^{-\beta(F'_1 + F'_2)}, \quad (2)$$

where the phase space integral has been done in two parts. Firstly, for each way of partitioning the particles between the two systems, the individual phase space integrals give the product of the individual partition functions. Secondly, and *crucially,* one must sum over the $N!/N_1! N_2!$ ways of partitioning the particles. Note that the individual distinguishability of particles is essential in this step. In quantum theory for indistinguishable particles, the counting procedure would be different because each state of the

system would be a superposition of states corresponding to the classical partitions.

Now *define* a conventional (extensive) free energy by

$$e^{-\beta F} = \frac{1}{N!} \int d\Gamma e^{-\beta H(\Gamma)}, \tag{3}$$

i.e., re-insert the $1/N!$ as though all particles are the same. Equation (2) can then be written as

$$e^{-\beta F} = \langle e^{-\beta(F_1+F_2)} \rangle_{\text{prtns}}, \tag{4}$$

where the average is taken over partitions with *equal a priori* probabilities. Traditional thermodynamics is recoverable from Eq. (4) if all particles are identical as far as their interactions are concerned, as then F_1 and F_2 depend only on N_1 and N_2 which are fixed, and the average is trivial: $F = F_1 + F_2$. Multicomponent thermodynamics for a finite number of species can be similarly derived. A key advantage of Eq. (4) appears though for polydisperse systems, since it leads to the generalisation of the entropy of mixing for moment variables.

In the example below, the excess free energy depends only on the mean size, which I shall denote m [i.e., $f_n(\sigma) = \sigma$]. The moment reduction will be to two density variables: ρ and $\rho m \equiv \phi$. To save on cumbersome notation, I will present results for this case only. All results can be generalized to the case of several moment variables, or polydispersity in more than one quantity.

Now, F' is essentially the excess free energy which is taken to depend on m only, and the same applies to F by construction. The average in Eq. (4) may therefore be taken by constraining the mean size:

$$e^{-\beta F} = \int dm_1 P(m_1) e^{-\beta(F_1+F_2)}, \tag{5}$$

where $P(m_1) = \langle \delta(m_1 - \sum_{i=1}^{N_1} \sigma_i/N_1) \rangle_{\text{prtns}}$ is the probability distribution for the mean size in the first system (m_1) taken over partitions with equal *a priori* probabilities (given m_1, the mean size in the second system is fixed by the moment equivalent of mass balance). Clearly, the combinatorial function $P(m_1)$ is the key to the problem. It appears in the joint free energy as a *combinatorial entropy*, $k_B \ln P(m_1)$, replacing the entropy of the mixing term.

An exact result for $P(m_1)$ will be described in a longer publication elsewhere [9]. It involves rather intractable integrals, and from a practical point of view it is not much use. In this Letter, I will confine myself to a much simpler but still very useful result which one obtains when the first subsystem is taken to be very much smaller than the second.

In this case, $P(m_1)$ becomes easier to calculate, as the σ_i in the small system may be treated as independent random variables. By writing the moment generating function of $P(m_1)$ as a product over moment generating functions of $p(\sigma)$, and evaluating the resulting integral by the saddle point method in the thermodynamic limit, one can show that the combinatorial entropy per particle is given by a Legendre transform: $\ln P(m_1)/N_1 = h(\theta) + m_1\theta$, where $m_1 = -\partial h/\partial \theta$. The function $h(\theta)$ is the cumulant generating function, defined by $e^{h(\theta)} = \int d\sigma p(\sigma) e^{-\sigma\theta}$ [10].

Table I gives the results for two standard distributions. It is interesting to see that the combinatorial entropy for a Gaussian distribution can be interpreted as an entropic spring which ties m to the mean size of the parent distribution [11]. The strength is inversely proportional to the variance of the parent distribution. For the Schulz distribution, note that the logarithmic divergence as $m \rightarrow 0$ prevents the mean size from becoming unphysically negative.

The limiting case described above gives exact results for two important classes of problems. The first is the thermodynamic stability of a homogeneous system (spinodal curves, critical points, etc.). This is exact because stability can be probed by allowing fluctuations to take place in a vanishingly small subregion. The second concerns the cloud and shadow curves. These are exact because, by definition, only an infinitesimal amount of a second phase has appeared. These arguments are qualitative, but formal proofs of the exactness of the present method in deriving these properties will be presented elsewhere [9].

Spinodal curves, critical points, cloud curves and shadow curves are of great interest in mapping out the phase behavior of new models, or old models extended to include polydispersity. The new method may therefore prove widely applicable and highly useful. It can be used approximately for full phase behavior calculations, too, by considering two (or more) small systems, each separately in equilibrium with a large (reservoir) system.

As an example of the method in action, I now consider polydisperse Flory-Huggins theory with a Schulz distribution as the parent distribution. Results derived previously using the traditional approach are recovered with ease. For this case, the free energy density (in units of $k_B T$) is

$$f = \rho \ln \rho + (1 - \phi) \ln(1 - \phi) + \chi\phi(1 - \phi)$$
$$- \alpha\rho \ln(\phi/\rho), \tag{6}$$

where ρ is the chain number density (nondimensionalized by the segment volume a^3), ϕ is the chain volume fraction,

TABLE I. Parent distribution $p(\sigma)$, cumulant generating function $h(\theta)$, and combinatorial entropy per particle $\ln P(m)/N$ for Gaussian and Schulz parent distributions. Constants and terms linear in the mean size m have been dropped from the combinatorial entropy.

$p(\sigma)$	$h(\theta)$	$\ln P(m)/N$
$\exp[-(\sigma - \overline{\sigma})^2/2\overline{v}]/\sqrt{2\pi\overline{v}}$	$\overline{\sigma}\theta + \overline{v}\theta^2/2$	$-(m - \overline{\sigma})^2/2\overline{v}$
$\sigma^{\alpha-1}e^{-\sigma/\beta}/\beta^\alpha\Gamma(\alpha)$	$-\alpha\ln(1 + \beta\theta)$	$\alpha\ln m$

and χ is Flory's χ parameter [2]. The first three terms in Eq. (6) are standard. The last term is the combinatorial entropy for the Schulz distribution (Table I). The advantage of the new approach is rapidly apparent, as the polydisperse problem has been reduced to two components, ρ and ϕ.

The spinodal curve (SC) and critical point (CP) conditions may be calculated from Eq. (6) via the usual determinant conditions [8]:

$$\frac{1}{1 - \phi} - 2\chi - \frac{\alpha}{\alpha + 1} \frac{\rho}{\phi^2} = 0 \quad \text{(SC)}, \qquad (7)$$

$$\frac{1}{(1 - \phi)^2} - \frac{\alpha(\alpha + 2)}{(\alpha + 1)^2} \frac{\rho}{\phi^3} = 0 \quad \text{(CP)}. \qquad (8)$$

These results should be supplemented by the constraint that $\phi = L_N\rho$, where $L_N = \alpha\beta$ is the mean or number average chain length for the parent distribution. This constraint must be imposed as the whole calculation is based on a combinatorial entropy which is derived from a given parent distribution. Applying the constraint and writing $L_W = (\alpha + 1)\beta$ and $L_Z = (\alpha + 2)\beta$ for the weight and Z-average chain lengths, respectively, give

$$\frac{1}{1 - \phi} - 2\chi - \frac{1}{L_W\phi} = 0 \quad \text{(SC)}, \qquad (9)$$

$$\frac{1}{(1 - \phi)^2} - \frac{L_Z}{L_W^2}\frac{1}{\phi^2} = 0 \quad \text{(CP)}. \qquad (10)$$

As promised, these are the exact results [2].

I have also calculated binodal curves in the (ϕ, ρ) plane numerically from the free energy Eq. (6) [12]. Figure 1 shows binodal curves, tie lines, spinodal curves, and critical points superimposed for three values of χ. The diagram gives an appealing geometric insight into the problem, for instance, the slope of the tie lines indicates a size partitioning effect, the more dense phase being enriched in long chains.
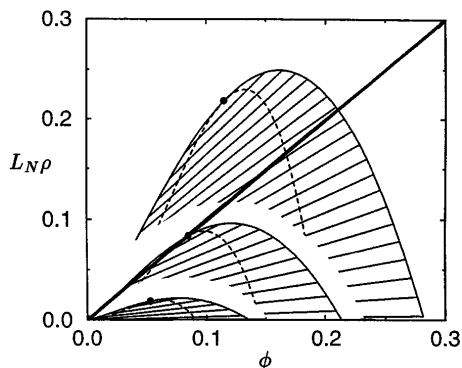
The heavy line in Fig. 1 is the physical $\phi = L_N\rho$ constraint. As discussed previously, only systems whose mean composition lies on this line are allowed. This means that not all of the phase behavior shown in Fig. 1 is accessible. The extremities of phase separation on the $\phi = L_N\rho$ line are points where phase separation just starts to occur, and the locus of these points in the physically accessible $(\phi = L_N\rho, \chi)$ plane is the cloud curve, shown in Fig. 2. The compositions of the phases that just start to appear as the cloud curve is passed do not, in general, lie in the physical plane (they are the compositions at the other ends of the cloud point tie lines in Fig. 1). These compositions may be projected onto the physical plane to give a shadow curve, by ignoring the value of ρ, for instance. The shadow curve obtained in this way for the present problem is also shown in Fig. 2.

Figure 2 also includes the spinodal stability curve and the critical point from Eqs. (9) and (10). The spinodal curve and the cloud curve touch at the critical point, which no longer lies at the minimum of either. This distorted behavior is a well-known feature of polydisperse systems. Here it is seen to be due to the way that *regular* phase behavior in (ϕ, ρ, χ) space is cut through by the physical constraint. The shadow curve also passes through the critical point. All the curves shown in Fig. 2 are exact, even though they have been constructed from phase behavior in Fig. 1, which is only an approximate projection of the true phase behavior of the fully polydisperse system.

Also shown in Fig. 2 is the phase behavior of the monodisperse polymer with chain length equal to L_N, the mean chain length in the polydisperse system. Comparing it with the cloud curve of the polydisperse system, the extent of phase separation is seen to be considerably enhanced in the latter–this is another well-known effect of polydispersity.

Returning to more general considerations, one can consider the effect of polydispersity on the *dynamics* of
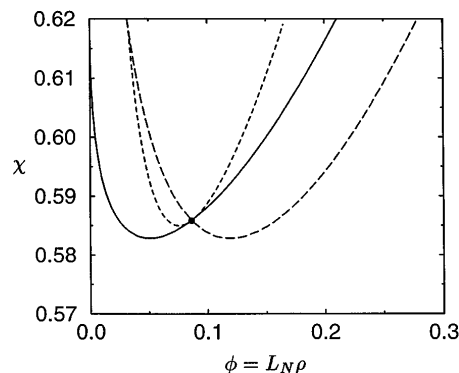

FIG. 1. Phase behavior of polydisperse Flory-Huggins theory in the (ϕ, ρ) plane for a Schulz distribution with $L_N = 100$, $L_W/L_N = 1.5$, for the free energy in Eq. (6). Shown superimposed, in order of increasing size, are two-phase regions for $\chi = 0.55$, 0.585, and 0.62. Binodals and tie lines are solid lines, spinodal curves are dashed lines. The physical $\phi = L_N\rho$ constraint is a thick solid line.

FIG. 2. A cut through the phase behavior in Fig. 1 by the physical $(\phi = L_N\rho, \chi)$ plane showing the cloud curve (solid line), shadow curve (long-dashed line), spinodal curve (dashed line), and the critical point. Also shown for comparison is the two phase region for the monodisperse Flory-Huggins theory with the same mean chain length, $L = 100$.

phase separation. Here, very little work appears to have been done. It is certainly not clear whether moment variables will prove to be as useful for analyzing the dynamics as they are in constructing the equilibrium phase behavior. A plausible scenario suggests itself though, on realizing that the overall density can be relaxed by collective particle motion much more easily than the moments. In a standard nomenclature, one might expect ρ to be a fast variable and the m_n to be slow variables. Phase separation might proceed in two stages: A fast density relaxation to a phase equilibrium dictated by quenching the moments to the mean values in the parent distribution, followed by a slow annealing of the moments (with ρ tracking them as a slaved variable), as the system moves towards the true free energy minimum. This area certainly warrants further investigation.

Finally, the present analysis throws an interesting sidelight on the Gibbs paradox, which suggests there should be an entropy of mixing on bringing into contact two systems of classically identical but distinguishable (or labeled) particles. Actually, such "experiments" are realized every day in computer simulations since the array index provides a label. An examination of Eqs. (3) and (4) indicates that, by the appropriate definitions, the entropy of mixing in such a case can be made to vanish. These definitions are rigorously based, and are the natural ones to ensure extensivity. Essentially, the same resolution is described by Jaynes [13], who pointed out that Gibbs himself had explained it, but in an untypically opaque manner [8]. It really turns on whether the particle labels can be coupled to an external variable or not. If they can't, one can define away the entropy associated with them.

After this work was nearly complete, I learned from P. Sollich and M. Cates [14] of an approach which, although based on distinctly different physical principles, is broadly equivalent to the one presented here. Proofs of this equivalence and further details of both methods will be presented elsewhere [9]. I thank them, and also

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