Analytic expression for the distribution of gel species in spatially homogeneous systems

LETTER TO THE EDITOR

Analytic expression for the distribution of gel species in spatially homogeneous systems

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Abstract. The equilibrium solution of the stochastic coagulation–fragmentation equations, for a spatially homogeneous system containing M monomers, is studied. If the coagulation–fragmentation rates K_{ij} and F_{ij} satisfy the condition $F_{ij}/K_{ij} = \lambda a_i a_j / a_{i+j}$ (needed to guarantee detailed balance) with $a_k \propto A k^{-\delta} z_c^{-k}$ and $2 < \delta < 3$, then the ensemble average size distribution $\langle x_k \rangle$ has a clearly bimodal character in the gel phase. The distribution of gel species is sharply peaked near $k = Mg$, where g is the gel fraction for the infinite system, with a width $\propto M^{1/(\delta-1)}$. The scaling function describing its precise shape is determined analytically. This function is highly non-symmetric; its second moment diverges.

In this letter the asymptotically exact distribution of gel species—i.e. the probability distribution for the size of the largest cluster—is derived for a class of equilibrium models of polymerisation. These models describe the formation and break up of clusters (macromolecules), distributed homogeneously in a volume V. The total number M of monomeric units is fixed. These units are distributed among clusters of various sizes. The microscopic state of the system is specified by the cluster size distribution $x = (x_1, x_2, \ldots, x_M)$ where x_k denotes the number of clusters containing k units (i.e. the number of k-mers) in the state x. This state may change under the influence of two basic processes: the formation of a cluster out of two smaller ones ('coagulation') and the break up of a cluster into two smaller ones ('fragmentation'). We assume that the corresponding reaction rates are such that the condition of microscopic detailed balance is satisfied. In that case we obtain [1, 9] the condition

$$F_{ij}/K_{ij} = \lambda a_i a_j / a_{i+j} \tag{1}$$

where F_{ij} and K_{ij} are the fragmentation and coagulation rates for a process involving one i-mer and one j-mer, and λ and a_k are numbers. Without loss of generality we may put $a_1 = 1$. The constant λ is then a measure of the fragmentation strength. The equilibrium probability distribution for microstates x may then be written as [1, 2]

$$P^{eq}(x) = \frac{1}{Z} \prod_{k=1}^{M} \frac{(\lambda V a_k)^{x_k}}{x_k!}. \tag{2}$$

We assume [1] the a_k to have the following asymptotic behaviour

$$a_k \simeq A k^{-\delta} z_c^{-k} \qquad k \to \infty \tag{3}$$

depending on the parameters A, δ and z_c (which are defined through this equation). For the so-called classical models of polymerisation [2–5, 9] $k! a_k$ can be identified

with the number of different ways of combining k monomers to build a k-mer [3]. For these models $\delta = \frac{5}{2}$. The thermodynamic limit is defined by taking $M \to \infty$, $V \to \infty$ keeping the parameter $q = \lambda V / M$ fixed. For $\delta > 2$, a phase transition occurs at a critical value q_c of q [1], with

$$q_c = \sum_{k=1}^{\infty} k a_k z_c^k = z_c F'(z_c) \tag{4}$$

where $F(z)$ is the generating function of the a_k [1, 3]

$$F(z) \equiv \sum_{k=1}^{\infty} a_k z^k. \tag{5}$$

This function has a singularity at $z = z_c$, on account of (3). For $q > q_c$, a cluster with a size $k = gM$ (the gel), proportional to the system size M, appears. The quantity g is called the gel fraction. It has been shown [1] from (2) that $g = 1 - q_c/q$. Here we show that for $q > q_c$, the ensemble average value of the cluster size distribution $\langle x_k \rangle = \sum_k x_k P^{eq}(x)$ has a bimodal character. It is a superposition of a distribution of sol species and a distribution of gel species (see figure 1). The latter is characterised by a maximum near $k = gM$ (with $g = 1 - q_c/q$). The width of this distribution scales as $M^{1/(\delta-1)}$, as $M \to \infty$, with δ as in (3). Its shape is described by a scaling function, which has some surprising properties: it is highly non-symmetric and its second moment diverges. This constitutes a generalisation of a result by Donoghue [4], valid for the aforementioned classical models.

From (2), an exact formula for the ensemble average size distribution can be derived [1], valid for finite M:

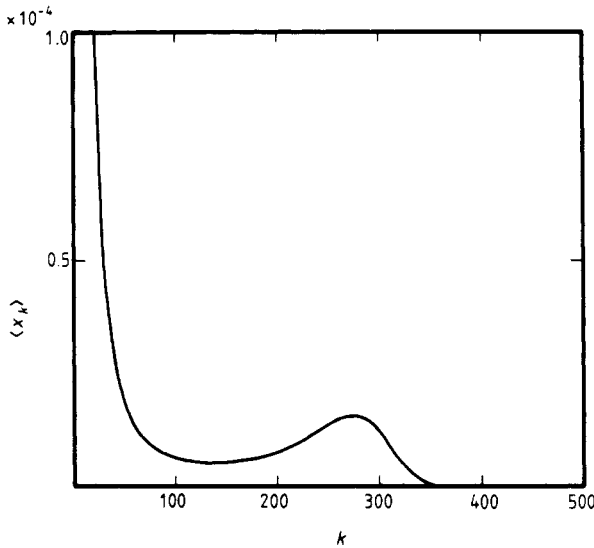$$\langle x_k \rangle = (M/q) a_k I_k / I_0 \tag{6}$$

Figure 1. The ensemble average number of clusters $\langle x_k \rangle$ calculated numerically from (6) for a system containing 500 monomers with $a_k = k^{-5/2}$ ($\delta = \frac{5}{2}$). Note the vertical scale. Already for $M = 500$ the distribution of gel species clearly emerges, showing a maximum near $k = Mg$ with $g = 1 - q_c/q$ (in the figure $q = 2q_c$). For $M \to \infty$ this maximum shifts to the right, whereby the distribution of sol and gel species become separated more clearly.

with

$$I_k = \oint \frac{\mathrm{d}z}{2\pi \mathrm{i}} \exp\left((k - M - 1)\log z + \frac{M}{q}F(z)\right) \tag{7}$$

where $F(z)$ was defined in (5). The integration path is a closed contour, close enough to the origin in the complex z plane. By partial integration one obtains a recursion relation for I_k, which can be solved numerically. A distinct distribution of gel species emerges even for small systems (see figure 1).

It is possible to derive the limiting form of the two component size distributions analytically, for large M. For fixed k and $M \to \infty$, the method of stationary phase [6] may be applied to (7). In this limit, the stationary points of the expression in the exponent are given through the equation $zF'(z) = q$. In the sol phase ($q < q_c$), there is always a solution $z = z_*$ to this equation lying inside the circle of convergence ($|z| < z_c$) of $F(z)$, as a consequence of (4) and (5). The one closest to $z = 0$ lies on the positive, real axis. The method of stationary phase, applied to (7), then yields for x_k in (6):

$$\langle x_k \rangle \simeq (M/q)a_k z_*^k \qquad k \text{ fixed}, M \to \infty, q < q_c. \tag{8}$$

This distribution contains all the mass, present in the system, since $\sum_k k\langle x_k \rangle = M$, as follows from the equation satisfied by z_*. It is valid in the sol phase ($q < q_c$), when there is no gel. For $k \to \infty$, this distribution behaves as constant $\times k^{-\delta}(z_*/z_c)^k$, i.e. it shows exponential decrease dressed with an algebraic prefactor.

For $q > q_c$, the above method fails, since z_* lies outside the circle of convergence of $F(z)$. In this case, we apply a somewhat different method. On account of (3), (4) and (5), $F(z)$ is singular in $z = z_c$ with the expansion

$$F(z) \simeq F_c + q_c \left(\frac{z - z_c}{z_c}\right) + A\Gamma(1 - \delta)\left(\frac{z_c - z}{z_c}\right)^{\delta - 1}$$
$$+ \mathrm{O}((z - z_c)^2) \qquad |z - z_c| \to 0, z - z_c \notin \mathbb{R}_+ \tag{9}$$

where we have assumed $2 < \delta < 3$ (for $\delta \le 2$, $q_c = \infty$ and no phase transition occurs). We deform the path of integration in equation (7) in such a way that it approaches the point $z = z_c$ along the ray $z - z_c \propto \mathrm{e}^{-\mathrm{i}\psi}$ (with ψ fixed) and leaves it along the ray $z - z_c \propto \mathrm{e}^{\mathrm{i}\psi}$. First we consider finite, fixed values of k and $q > q_c$. Then it can be shown, if ψ is chosen within the range $[\frac{1}{2}\pi(\delta - 1)^{-1}, \frac{3}{2}\pi(\delta - 1)^{-1}]$, that for $M \to \infty$ the asymptotic dominant contribution to the integral comes from the immediate neighbourhood of $z = z_c$, so that for $F(z)$ its expansion about $z = z_c$, (9) can be substituted. After some algebra, this yields

$$I_k \simeq (A/q) \, \mathrm{e}^{(M/q)F_c} z_c^{k-M-1} M^{1-\delta} g^{-\delta} \qquad M \to \infty. \tag{10}$$

Here $g = 1 - q_c/q$ is the gel fraction, $F_c \equiv F(z_c)$ and the parameters A, δ and z_c are as in (3). Hence, using (6)

$$\langle x_k \rangle \simeq (M/q)a_k z_c^k \qquad k \text{ fixed}, M \to \infty, q > q_c \tag{11}$$

represents the distribution of sol species in the gel phase. This distribution does not contain all the mass in the system, as follows from (4) and (5). The 'missing mass' $(1 - q_c/q)M$ is in the gel.

Next we derive the asymptotic form of the distribution of gel species. Since this distribution is sharply peaked about $k = Mg$, for large M, we introduce a parameter y

through the equation: $k = Mg + M^\alpha y$ where $\alpha(<1)$ is a parameter for the width of the peak, to be determined. Again, choosing ψ in the range specified above, one shows that for fixed y the dominant contribution to I_k comes from the immediate neighbourhood of $z = z_c$. The value of α is determined from the condition that this contribution depends on y in a non-trivial way (i.e. that it is not equal to a constant, or zero or infinite). One finds $\alpha = (\delta - 1)^{-1}$. For this value of α a non-trivial y dependence is derived by substituting (9) into (7) and expanding about $z = z_c$. The term linear in $u = z - z_c$ disappears for $g = 1 - q_c/q$ and the term proportional to u^2 becomes confluent with the term containing y, as $M \to \infty$. The result, combined with (10) for $k = 0$, substituted into (6)—where a_k may now be replaced by its asymptotic behaviour, (3)—can be written in the form

$$\langle x_k \rangle = (qM/A)^{-1/(\delta-1)} \cdot G_\delta((q/A)^{1/(\delta-1)} \cdot y) \qquad k = Mg + yM^{1/(\delta-1)}, \ M \to \infty, \ y \text{ fixed} \tag{12}$$

where $G_\delta(y)$ is a scaling function, describing in detail the distribution of gel species. An explicit formula for $G_\delta(y)$ is the following

$$G_\delta(y) = \frac{1}{2\pi i} \int_{-i\infty}^{i\infty} dt \exp(yt + \Gamma(1-\delta)(-t)^{\delta-1}). \tag{13}$$

This expression follows by taking the path of integration in (7) at right angles to the real axis ($\psi = \pi$) through the point $z = z_c$ and subsequently substituting $z - z_c = tM^{-1/(\delta-1)}$, keeping the dominant contribution for $M \to \infty$.

Typically, the graph of $G_\delta(y)$ has a shape as in figure 2 (which corresponds to numerical calculations for $\delta = 2.2$ and $\delta = 2.5$). It has a maximum for some positive y value, which shifts to the right with decreasing δ. Using standard methods, one derives the following properties: $\int_{-\infty}^{\infty} G_\delta(y) \, dy = 1$ (this corresponds to the fact that
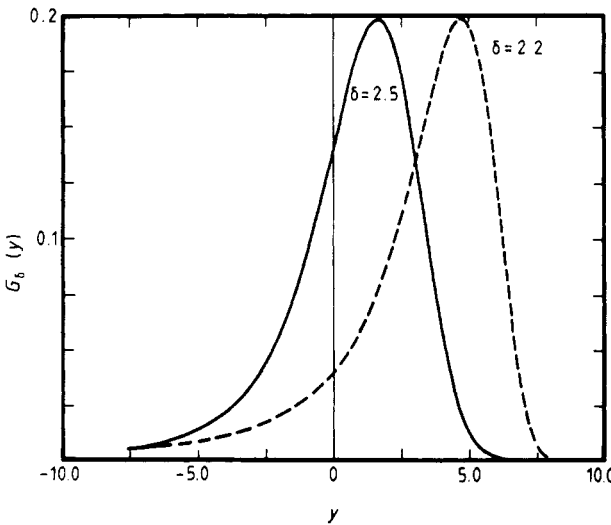

Figure 2. Plot of the scaling function $G_\delta(y)$ as a function of the scaling variable y, describing the exact shape of the limiting distribution of gel species, for two values of δ: $\delta = 2.2$ (broken curve) and $\delta = 2.5$ (full curve). Note the asymmetric character of $G_\delta(y)$, showing algebraic decay $\simeq (-y)^{-\delta}$ for $y \to -\infty$ and superexponential decrease for $y \to +\infty$. The second moment of $G_\delta(y)$ diverges, since $2 < \delta < 3$.

the gel contains a single cluster), $G_\delta(y) \simeq (-y)^{-\delta} (y \to -\infty)$, and $G_\delta(y) = C_1 y^\mu \exp(-C_2 y^\nu) (y \to +\infty)$ where $\mu = \frac{1}{2}(3-\delta)/(\delta-2)$, $\nu = (\delta-1)/(\delta-2)$ and the constants C_k are more complicated, known functions of δ. Note the highly asymmetric character of the distribution. For $\delta = \frac{5}{2}$, (1) is in agreement with a corresponding result of Donoghue [3]. As $M \to \infty$, (12) and (13) also describe the probability distribution for the size of the largest cluster in the gel phase. The properties of the scaling function, notably the divergence of its second moment, have some interesting consequences. Suppose one deals with a system, similar to the one discussed in this letter, but for which no analytic expressions such as (6) can be derived. An example might be given by the problem of percolation on a d-dimensional lattice. Suppose further that one wants to determine the gel fraction numerically. In a typical Monte Carlo experiment one would simply determine the size of the largest cluster, k_{max}, N times and calculate the average value $\bar{g} = (1/NM) \Sigma_n k_{max}^{(n)}$. For the exactly soluble problem discussed in this letter, it follows from (12) and (13) that this quantity is itself distributed about $\bar{g} = g(=1 - q_c/q)$, with a distribution of exactly the same shape as in figure 2 (13), but with a width $\propto (MN)^{(2-\delta)/(\delta-1)}$. Note that the dependence on N is not $\propto N^{-1/2} (N \to \infty)$. This is due to properties of $G_\delta(y)$. These render the central limit theorem [8] invalid for this case. If this kind of behaviour would also occur for the abovementioned systems, where one has to resort to numerical methods to determine the gel fraction g, then that would imply that the error bars are much larger than customarily expected (especially for δ near 2).

It would, therefore, be of interest to determine the distribution of k_{max} and its scaling properties for these non-analytically soluble problems. In summary, at least for the system discussed in this letter, the gel fraction for large but finite systems fluctuates asymmetrically about its mean value, with a width $M^{1/(\delta-1)}$, where δ is defined through (3), described by the scaling function (13), whose second moment diverges. Details of the calculation will be published elsewhere.

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