Number of configurations of a linear polymer

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Let us denote by Γ_N the phase volume of configurations of a linear polymer of polymerization index (number of monomers) N. For large N, it behaves as

$$\Gamma_N \sim z_{\rm c}^{-N} N^{\gamma-1}. \qquad (1)$$

The corresponding generating function is given by

$$\Gamma(z) := \sum_{N=0}^{\infty} z^N \Gamma_N = \psi(z) + \text{const.} \times \sum_{N=1}^{\infty} \left(\frac{z}{z_{\rm c}}\right)^N \cdot \frac{1}{N^{1-\gamma}} = \psi(z) + \text{const.} \times \phi_{1-\gamma}\left(\frac{z}{z_{\rm c}}\right), \qquad (2)$$

where $\psi(z)$ is a regular function which takes into account the behavior for small values of N and $\phi_\alpha(z)$ is the polylog function:

$$\phi_\alpha(z) := \sum_{N=1}^{\infty} \frac{z^N}{N^\alpha}. \qquad (3)$$

In the following we shall neglect the inessential function $\psi(z)$ and set the constant to 1. The polylog function has a singularity for $z \to 1$, therefore $\Gamma(z)$ is singular for $z \to z_{\rm c}$. To evaluate its behavior near the singularity, we define $w = -\ln(z/z_{\rm c})$. Then for small values of w we can approximate the sum by an integral:

$$\phi_{1-\gamma}(w) := \Gamma(z_{\rm c}\,{\rm e}^{-w}) \simeq \int_1^\infty {\rm d}N\ {\rm e}^{-Nw} N^{\gamma-1}. \qquad (4)$$

By the change of variable $u = Nw$ we obtain

$$\phi_{1-\gamma}(w) \simeq w^{-\gamma} \int_w^\infty {\rm d}u\ {\rm e}^{-u} u^{\gamma-1}. \qquad (5)$$

The integral yields $\Gamma_{\rm E}(\gamma)$ for $w \to 0$, where $\Gamma_{\rm E}(z)$ is Euler's gamma function. Thus we have obtained

$$\Gamma(z) \simeq \Gamma_{\rm E}(\gamma)\left[-\ln\left(\frac{z}{z_{\rm c}}\right)\right]^{-\gamma} \simeq \Gamma_{\rm E}(\gamma)\left(1 - \frac{z}{z_{\rm c}}\right)^{-\gamma}. \qquad (6)$$

To obtain the reverse relation, let us consider near $z = z_{\rm c}$ the function

$$\Gamma(z) \simeq \Gamma_{\rm E}(\gamma)\left(1 - \frac{z}{z_{\rm c}}\right)^{-\gamma}. \qquad (7)$$

We then have

$$\begin{aligned}\Gamma(z) &= \Gamma_{\rm E}(\gamma) \sum_{N=0}^{\infty} \binom{-\gamma}{N} \left(-\frac{z}{z_{\rm c}}\right)^N = \Gamma_{\rm E}(\gamma) \sum_{N=0}^{\infty} \frac{(-\gamma)(-\gamma-1)\cdots(-\gamma-N+1)}{N!}\left(-\frac{z}{z_{\rm c}}\right) \\ &= \Gamma_{\rm E}(\gamma) \sum_{N=0}^{\infty} \frac{\gamma\,(\gamma+1)\cdots(\gamma+N-1)}{N!}\left(\frac{z}{z_{\rm c}}\right)^N = \sum_{N=0}^{\infty} \frac{\Gamma_{\rm E}(\gamma+N)}{\Gamma_{\rm E}(N+1)}\left(\frac{z}{z_{\rm c}}\right)^N \\ &= \sum_{N=0}^{\infty} \mathcal{Q}_N \left(\frac{z}{z_{\rm c}}\right)^N. \end{aligned} \qquad (8)$$

For large values of N, using Stirling's formula, we obtain

$$\begin{aligned}
\mathcal{Q}_N := \frac{\Gamma_{\mathrm{E}}(\gamma+N)}{\Gamma_{\mathrm{E}}(N+1)} &\simeq \frac{(\gamma+N-1)^{\gamma+N-1}\mathrm{e}^{-(\gamma+N-1)}\sqrt{2\pi(\gamma+N-1)}}{N^N\mathrm{e}^{-N}\sqrt{2\pi N}} \\
&\simeq \frac{(\gamma+N-1)^{\gamma+N-1}}{N^N}\mathrm{e}^{1-\gamma}\left(1+\frac{\gamma-1}{N}\right)^{\frac{1}{2}} \\
&\simeq N^{\gamma-1}\left(1+\frac{\gamma-1}{N}\right)^{N}\mathrm{e}^{1-\gamma}\left(1+\frac{\gamma-1}{N}\right)^{\gamma-\frac{1}{2}}.
\end{aligned} \tag{9}$$

For $N \to \infty$, hte last factor approaches 1 and the second one approaches $\mathrm{e}^{\gamma-1}$. Thus we have, for large values of N,

$$\mathcal{Q}_N \simeq N^{\gamma-1}, \tag{10}$$

and therefore

$$\Gamma_N \simeq z_{\mathrm{c}}^{-N}N^{\gamma-1}. \tag{11}$$

The second result can also be obtained as follows. Assume that

$$\Gamma(z) \sim \left(1-\frac{z}{z_{\mathrm{c}}}\right)^{-\gamma}. \tag{12}$$

We wish to evaluate the behavior of Γ_N for $N \gg 1$. We have

$$\Gamma_N = \frac{1}{2\pi}\oint \mathrm{d}z\, \frac{\Gamma(z)}{z^{N+1}}. \tag{13}$$

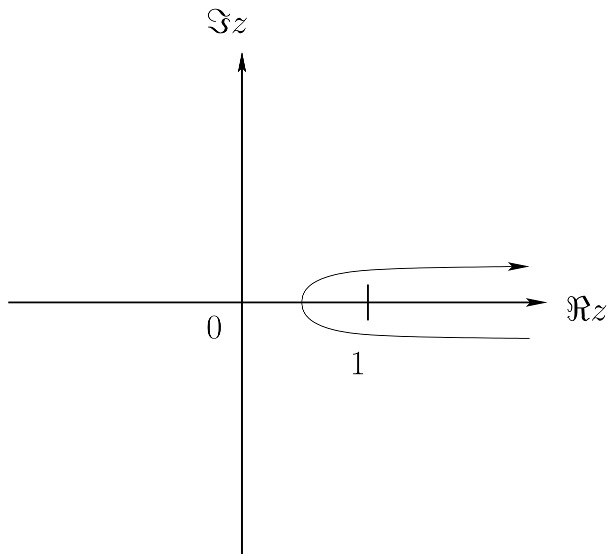
We then have

$$\Gamma_N \simeq \frac{1}{2\pi}\oint \mathrm{d}z\, \frac{(1-z/z_{\mathrm{c}})^{-\gamma}}{z^{N+1}}. \tag{14}$$

Substituting $z = y\, z_c$ we have

$$\begin{aligned}
\Gamma_N &\simeq \frac{1}{2\pi}\oint \mathrm{d}y\, (1-y)^{-\gamma}(y z_{\mathrm{c}})^{-N-1}z_{\mathrm{c}} \\
&= z_{\mathrm{c}}^{-N}\oint \mathrm{d}y\, (1-y)^{-\gamma}y^{-N-1}
\end{aligned} \tag{15}$$

Consider the contour shown below.



Set $y = 1 + t/N$, with $0 \leq t < +\infty$. We have

$$\Gamma_N \simeq z_{\rm c}^{-N} N^{\gamma-1} \int_0^\infty {\rm d}t \; t^{-\gamma} \left(1 + \frac{t}{N}\right)^{-N-1} \simeq z_{\rm c}^{-N} N^{\gamma-1} \int_0^\infty {\rm d}t \; t^{-\gamma} {\rm e}^{-t} \propto z_{\rm c}^{-N} N^{\gamma-1}. \qquad (16)$$