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Long-range correlation effects in directional living polymers

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Abstract

The statistics of (equilibrium) living polymers including both linear chains and rings are considered theoretically. Particular attention is addressed to directional polymers characterized by an arrow along the backbone defined by its chemical structure. Thermodynamic and correlation properties of living polymers are studied both in the mean-field and in the critical scaling regimes. It is shown that living polymers with no rings, classical living polymers with rings, and directional living polymers with rings form three distinct classes characterized by different critical exponents and qualitatively different long-range correlation functions.

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1. Introduction

In contrast to classical polymers, the molecular weight of living (or equilibrium) polymers is not fixed: their polymerization is reversible.[1] Living polymers include wormlike surfactant micelles,[2] columnar structures of discotics,[3,4] reversibly polymerizing organic chains, various dynamic and supramolecular polymers,[5–9] including biological fibrillar structures of peptides and proteins (like tubulin filaments).[10–12] Unlike classical polymers involving only permanent, covalent chemical bonds along their backbone, living chains often involve reversible bonds based on metal-ligand coordination or multiple H-bonds, imine bonds, $\pi-\pi$ stacking interactions, etc.[5,7,6] As a result, living polymers can grow or disassemble spontaneously responding to external triggers.

In many cases living polymers can also form competing cyclic structures along with linear chains.[13] The rings proved to be of importance for both equilibrium and dynamic properties of living polymer systems.[14–19] In particular, Petschek, Pfeuty and Wheeler[20] have shown that the presence of rings qualitatively affects the equilibrium behavior of the system (osmotic pressure, chain length) near the polymerization transition.

The structure of simple polymer chains like polyethylene or polystyrene does not distinguish between forward and backward direction along the polymer backbone. However, polymers with more complicated structure of a repeat unit permit to distinguish between the two opposite senses of direction along the chain. Important examples are provided by proteins, and by their simpler analogs, homopeptides (Fig. 1). In fact, an arrow along the backbone (from, say, CO to NH group) is inherent in the peptide structure: peptide chains are always directional. Besides, peptides and proteins can form cyclic structures (peptide rings). However, polypeptides are not living chain structures. Polymer structures that are both living (reversible) and directional can be found among supramolecular polymers.[5,6,8,21] In general, any head-to-tail reversible self-assembly of asymmetric units gives a directional structure (Fig. 2). A more specific example of an asymmetric unit for directional supramolecular self-assembly based on triple H-bond manifolds is shown in Fig. 3. Other examples of such structures involving 3-fold intermolecular H-bonds, including helical columns of benzene trisamides with uni-directional hydrogen bonding, can be found in ref.[21] (see Fig. 23 there).

There exist many more examples of supramolecular directional chains. An interesting example is provided by the so-called supramolecular daisy chains[22,23] based on 'topological' guest-host complex between a rod-shaped 'tail' of one molecular unit and a ring-shaped cavity of another identical unit. The recognition between the tail and the ring is hinged on H-bonds augmented by $\pi-\pi$ stacking interactions.[24] Another important class of directional living chains is provided by protein biopolymers. While proteins themselves are not living (reversible) structures, the folded proteins can aggregate forming supramolecular polymers. This ability of proteins to self-assemble is widely exploited in nature to create various subcellular structures. The most important protein polymers are bacterial flagella, microtubules and F-actin.[10] All these biological supramolecular polymers exhibit directional chain structure: their two ends are physically different, and their building blocks (protein unimers) are polar. Notably, F-actin, often shows circular (ring-like) structures in addition to linear filaments.[25]

Equilibrium polymerization (self-assembly of living chains) can be described as a smeared second-order phase transition.[26,27,20,10] The transition width is related to the length of living chains: the longer are the chains, the more narrow is the transition. In turn, the chain length N is defined by the energy penalty for the chain end (end-cap energy E): the equilibrium chains grow very long if this energy is high. In the limit $N \to \infty$ the system near the polymerization transition exhibits strong concentration fluctuations and other properties typical for critical phenomena associated with a second-order transition (diverging scattering functions, compressibility, heat capacity)[28–30,27]. Such a behavior is typical for equilibrium polymerization both with and without rings.[30,27,20] However, the critical exponents are different in the two cases.[20]

In this paper we analyze equilibrium properties of living polymers, in particular, for the case of directional living polymers allowing ring formation, which was virtually not considered before. It is revealed that, according to their correlation properties, these systems are qualitatively different from the classical living polymer (with or without rings) both near and far beyond the polymerization transition threshold.

The model and its mean-field behavior are considered in the next two sections. Polymer correlation functions (including correlations of the total concentration) are considered in the mean-field regime in sections 3 and 4. It is shown that, unlike classical living polymers with rings, directional polymers are characterized by long-range correlation effects, including polymer-induced interactions at distances well beyond the classical correlation length ξ corresponding to the Flory-Edwards screening. Such behavior resembles that inherent in systems of permanent polymer chains[31,32]. The nature of these effects is further highlighted in the last section (Conclusions) and in Appendix A. The properties of the living polymers in the critical regime near the polymerization transitions are considered in section 5. The ensemble of the results (the basic scaling laws, correlation functions, chain-length distributions) are further generalized and summarized in section 6.

2. The model and the polymer-magnetic analogy.

In this section we specify the general model of living polymers and establish a convenient analogy between the polymer model and the O(n) model of magnetism. The mapping we use is akin to, but different from, that was considered in the previous works.[20]

We adopt the following lattice model of living polymers (Fig. 4): Each chain is a sequence of units connected by bonds. The units occupy different sites on a cubic lattice $\{r_i\}$. The statistical weight of a bond between sites r_i, r_j is $K_{i,j} = K_{\underline{s}}$, where $\underline{s} = \underline{r}_{ij} \equiv \underline{r}_i - \underline{r}_j$. The function K_s is localized within the typical bond length b: $|s| \lesssim b$; it is normalized for simplicity:

$$\sum_{\underline{s}} K_{\underline{s}} = 1$$

Thus, the statistical weight of a linear chain occupying sites r_1, r_2, ..r_N is $Z_l = h^2\beta^N K_{1,2}K_{2,3}..K_{N-1,N}$, where h is the statistical weight of an end unit and β is the activity of any other monomer unit. If a chain forms a ring its statistical weight becomes $Z_c = n\beta^N K_{1,2}K_{2,3}..K_{N-1,N}K_{N,1}$, where n is the weight factor attributed to each cycling chains. The grand canonical partition function of the living polymer system is

$$Z(\beta,h)=\sum_{\mathcal{N}_m,\mathcal{N}_l,\mathcal{N}_r}\beta^{\mathcal{N}_m}n^{\mathcal{N}_r}h^{2\mathcal{N}_l}C_p\left(\mathcal{N}_m,\mathcal{N}_l,\mathcal{N}_r\right) \tag{1}$$

where $C_p\left(\mathcal{N}_m,\mathcal{N}_l,\mathcal{N}_r\right)$ is the K-weighted number of different configurations of self-avoiding polymers involving $\mathcal{N}_m$ monomer units forming $\mathcal{N}_l$ linear chains and $\mathcal{N}_r$ cycles (double occupancy of sites is not allowed).

This model generalizes the lattice polymer models used before[31,20] as it allows for arbitrary bonds not necessarily connecting the nearest-neighboring sites. In this case the model can be made continuous by reducing the lattice spacing while keeping the bond length b.

Obviously, the case $n=0$ describes the system of just linear living chains with scission energy $2E$ such that $e^{-2E}=h^2$ (here and below k_BT is considered as the energy unit). Further, $n=1$ corresponds to classical living polymers including rings, while the directional polymers correspond to $h^2=2e^{-2E}$ and $n=2$ (here the prefactor '2' accounts for two distinct directions along the chain).

To establish the analogy with O(n) magnetic systems we first note, following refs.[31–34], the exact formal relation

$$\prod_i\left(1+\beta h\frac{\partial}{\partial\psi_{1i}}+\frac{\beta}{2}\frac{\partial^2}{\partial\psi_{\alpha i}\partial\psi_{\alpha i}}\right)e^{\widetilde{H}[\psi]}\bigg|_{\psi=0}=Z(\beta,h) \tag{2}$$

where Z is defined in eq. (1), $\psi=\{\psi_{\alpha i},\alpha=1,..n\}$ is the auxiliary n-component vector field,

$$\widetilde{H}\left[\psi\right]=\frac{1}{2}\sum_{i,j}K_{i,j}\psi_{\alpha i}\psi_{\alpha j}$$

and summation over repeated α is always assumed. [1]

Next we recall the Stratonovich-Hubbard transformation:

$$\int e^{\varphi\cdot\psi-H_0[\varphi]}\mathcal{D}\left[\varphi\right]=\text{const}\,e^{\widetilde{H}[\psi]} \tag{3}$$

where $\varphi=\{\varphi_{\alpha i},\alpha=1,..n\}$ is another auxiliary n-vector field, $\varphi\cdot\psi\equiv\sum_i\varphi_{\alpha i}\psi_{\alpha i}$,

$$H_0\left[\varphi\right]=\frac{1}{2}\sum_{i,j}K_{i,j}^{-1}\varphi_{\alpha i}\varphi_{\alpha j}$$

and K^{-1} is the matrix inverse to K. On using eqs. (2), (3) we get[31,32]

$$Z(\beta,h)=Z_m(\beta,h)/Z_m(0,0), \tag{4}$$

where the magnetic partition function is

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[1] Chains of 1 unit are not allowed. Chains of two units (dimers) are special: they can be considered as linear chains and as minimal cycles. Accordingly, the total statistical weight of a dimer (i,j) is $\beta^2\left(h^2K_{i,j}+\frac{n}{2}K_{i,j}^2\right)$.

$$Z_m = \int e^{-H_m[\varphi]} \mathcal{D}[\varphi]$$

$$H_m[\varphi] = H_0[\varphi] + H_1[\varphi], \quad H_1[\varphi] = -\sum_i \ln\left(1 + \beta h \varphi_{1i} + \frac{\beta}{2}\varphi_{\alpha i}\varphi_{\alpha i}\right) \tag{5}$$

Thus, for the magnetic system (eq. (5)) β plays the role of the interaction parameter, and h corresponds to the magnetic field.

Several notes are relevant here. First, eq. (3) implies that the matrix K must be positively defined demanding that $K_{i,i} \equiv K_0 > 0$. More precisely, the magnetic function Z_m is defined for positive and sufficiently large K_0. By contrast, it is convenient to set $K_0 = 0$ for the polymer model. This does not make a problem: we simply consider the analytical continuation of the function on the r.h.s. of eq. (4) for small K_0 (down to $K_0 = 0$). This continuation is unique: indeed, based on eq. (2), it can be shown that a change of K_0 is equivalent to a simple renormalization of β: $1/\beta \rightarrow 1/\beta + nK_0/2$. Therefore, we formally set $K_0 = 0$ in what follows.

Second, the magnetic Hamiltonian (5) may seem to be non-local. The problem, however, is easily removed by the substitution

$$\varphi_{\alpha i} = \sum_{i,j} K_{i,j} \cdot \sigma_{\alpha j} \tag{6}$$

where σ can be viewed as the n-vector field of spins. Then, H_m in terms of σ is explicitly local [2] and, moreover, is equivalent at large length-scales to the classical n-component spin model described by the Ginzburg-Landau Hamiltonian. As for the field φ, it can be physically viewed as the molecular magnetic field due to the spins. [3]

The magnetic model defined above is significantly different from those used in refs.[20],[35]. The polymer-magnetic analogy described above is both simple and exact, it allows to study both mean-field and critical fluctuation regimes for living polymers within a well-defined common framework. In the next section we first demonstrate that our model provides correct statistical description of living polymer systems at the mean-field level, in agreement with the classical results[36–41]. This part is followed by an analysis of the weight concentration of rings, and of the correlation properties of living polymers in the mean-field regime.

3. Mean-field free energy, chain length, fraction of rings, and correlation functions

3.1. Free energy

Let us calculate the grand thermodynamic potential (per site), $F = -\frac{1}{\mathcal{N}} \ln Z$, of the living polymer model described above ($\mathcal{N}$ is the total number of sites).

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[2] Note that the Hamiltonian H_m, when expressed in terms of σ, does not involve K^{-1}. For example, $H_0 = \frac{1}{2}\sum_{i,j} K_{i,j}\sigma_{\alpha i}\sigma_{\alpha j}$.

[3] Note that there is little difference between φ and σ at length-scales $\gg b$.

Eq. (4) implies that $F(\beta, h) = F_m(\beta, h) - F_m(0,0)$, where $F_m = -\frac{1}{\mathcal{N}} \ln Z_m$. To find F_m we follow the mean-field approach,[31,34] which is valid if the number of ways each site can be bonded with its neighbors is large. It is convenient to define the effective number of neighbors

$$z^* = \left(\sum_s K_s\right)^2 / \sum_s K_s^2$$

Note that $z^* \sim b^3$. The mean-field approximation, which is applicable for $z^* \gg 1$, can be reduced to minimization of H_m:

$$F_m(\beta, h) \simeq \frac{1}{\mathcal{N}} \min H_m(\beta, h)$$

The minimum corresponds to a uniform field[31,34] $\varphi_{\alpha i} = m\delta_{\alpha 1}$. The result for $h = 0$ is simple:

$$m = 0, \quad F = F_m(\beta, 0) - F_m(0,0) = 0 \quad \text{for } \beta < 1,$$

$$m = \sqrt{2(1 - 1/\beta)}, \quad F = 1 - 1/\beta - \ln\beta \quad \text{for } \beta > 1 \tag{7}$$

Note that the result is independent of the weight of rings (i.e., of n), as anyway the rings are asymptotically rare in the mean-field regime (their probability is $\sim 1/z^*$). Thus, $\beta = 1$ is the critical mean-field threshold for the magnetization transition, which corresponds to the onset of the polymerization for the living polymer system. Indeed, as follows directly from eq. (1), the fraction of sites occupied by monomer units is

$$\phi \equiv \mathcal{N}_m/\mathcal{N} = -\frac{\partial F}{\partial \ln\beta} \tag{8}$$

On using eqs. (7) we get

$$\phi = 0, \ \ \beta < 1; \ \ \phi = 1 - 1/\beta, \ \ \beta > 1 \tag{9}$$

These mean-field results can be verified by direct calculation of the polymer configuration function $C_p(\mathcal{N}_m) = e^{-\mathcal{N} f_p(\phi)}$. [4] To calculate the free energy $f_p(\phi)$ per monomer unit of the system of infinite linear chains (finite linear chains are not allowed for $h = 0$), we note that the conformational contribution in f_p is just zero since the statistical weight per bond, $\sum_s K_s = 1$, while the ideal-gas free energy also vanishes since the chains are infinite. Hence

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[4] There are no rings in the basic mean-field approximation: the volume concentration of rings $\phi_r = 0$. A more precise result, $\phi_r \sim 1/z^*$ (a unit volume is attributed to a monomer unit), comes as a fluctuation correction (cf. eq. (32) below). Therefore, the total concentration $\phi = \phi_r + \phi_l$, where ϕ_l is the volume concentration of linear chains, does not vanish at the polymerization transition point $\beta = \beta^* \simeq 1$: it is $\phi_l = 0$ at $\beta = \beta^*$. So, it is appropriate to replace ϕ with ϕ_l and β with β/β^* in eqs. (9). Note that a fluctuation correction also applies to β^*: $\beta^* - 1 \simeq \phi_r \sim 1/z^*$. The total concentration is still $\phi \simeq 1 - 1/\beta$ for $\beta > \beta^*$ as a result of some compensation of the corrections.

$$f_p = \phi + (1-\phi)\ln(1-\phi) \tag{10}$$

which is the lattice-gas interaction energy per site. The above equation is based on the mean-field approximation; it is valid if[43,44]

$$\phi_l \gg 1/z^{*2} \tag{11}$$

(note that the monomer excluded volume is $v_{cell} = 1$, and $v_{cell}/b^3 \sim 1/z^*$). In the macroscopic limit the grand polymer thermodynamic potential (corresponding to $Z = \sum_{\mathcal{N}_m} \beta^{\mathcal{N}_m} C_p(\mathcal{N}_m)$) can be found as

$$F = \min_{\phi}\left[-\phi\ln\beta + f_p(\phi)\right]$$

giving

$$\phi = 1 - 1/\beta \quad \text{and} \quad F = 1 - 1/\beta - \ln\beta$$

in agreement with eq. (7).

So far we assumed that $h = 0$. For small $h > 0$ we get

$$F \simeq 1 - \frac{1}{\beta} - \ln\beta - h\sqrt{2(1-1/\beta)}, \quad h \ll 1, \ \ \beta > 1 \tag{12}$$

instead of eq. (7), and:

$$\phi \simeq 1 - \frac{1}{\beta} + \frac{h}{\sqrt{2\beta(\beta-1)}}, \quad h \ll 1, \ \ \beta > 1$$

The h-correction to ϕ (and ϕ_l) is thus increasing near the transition point ($\beta = 1$). Demanding that the correction is smaller than ϕ_l we get the additional condition $h \ll \phi_l^{3/2}$.

3.2. Chain length

As follows from eq. (1), the mean number of linear chains is $\langle \mathcal{N}_l \rangle = \frac{1}{2}\frac{\partial \ln Z}{\partial \ln h}$, and their concentration is

$$c_l = -\frac{1}{2}\frac{\partial F}{\partial \ln h} \tag{13}$$

Eq. (12) and the mean-field result, $\phi_l \simeq 1 - 1/\beta$ for $\beta > 1$, then lead to $c_l \simeq h\sqrt{\phi_l/2}$ for $h \ll 1$. Therefore, the mean polymerization index of linear chains is

$$N_m = \phi_l/c_l \simeq \sqrt{2\phi_l}/h, \quad h \ll 1 \tag{14}$$

Thus, we recover the classical $\sqrt{\phi_l}$ law for the chain length.

The length distribution of linear chains is nearly exponential [5] in the mean-field regime (the Flory distribution[42]):

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[5] It reflects strong screening of excluded-volume interactions in concentrated polymer solutions and melts.

$$c_l(N)/c_l \simeq \delta e^{-N\delta} \tag{15}$$

where $\delta \simeq 1/N_m$.

Replacing F with F_m in eq. (13) we get the general expression for c_l in magnetic terms

$$c_l = h\left\langle \frac{\varphi_1}{2/\beta + 2h\varphi_1 + \varphi^2} \right\rangle \tag{16}$$

where $\varphi_1 = \varphi_{1i}$ and $\varphi^2 = \varphi_{\alpha i}\varphi_{\alpha i}$ for any site i. Similarly, using eq. (8) we get the total monomer concentration

$$\phi = \left\langle \frac{\varphi^2}{2/\beta + 2h\varphi_1 + \varphi^2} \right\rangle + 2c_l \tag{17}$$

The two terms in the r.h.s. are the concentrations of internal and end monomers, respectively. The second term, $2c_l$, is subdominant for $N_m \gg 1$.

3.3. Fraction of rings

In the general case both linear chains and rings are present in the system:

$$\phi = \phi_l + \phi_r$$

where $\phi_l = \mathcal{N}_{ml}/\mathcal{N}$ is number concentration of all monomers belonging to linear chains, and $\phi_r = \mathcal{N}_{mr}/\mathcal{N}$ is the similar quantity for rings ($\mathcal{N}_{mr}$ is the total number of all monomers in the rings, $\mathcal{N}_m = \mathcal{N}_{ml} + \mathcal{N}_{mr}$). To find ϕ_r, we modify the magnetic Hamiltonian H_m, following ref.[20], introducing the magnetic anisotropy.

To this end, we replace $\frac{\beta}{2}\varphi_{\alpha i}\varphi_{\alpha i}$ in eq. (5) with $\frac{\beta}{2}\left(\varphi_{\alpha i}\varphi_{\alpha i}\left(1-\frac{g}{n-1}\right)+\frac{ng}{n-1}\varphi_{1i}^2\right)$. The corresponding modification of the polymer partition function, eq. (1), is simple: the weight of each ring, $n\beta^N$, is now replaced by $\left[(1+g)^N + (n-1)\left(1-\frac{g}{n-1}\right)^N\right]\beta^N = n\beta^N\left(1+\mathcal{O}(g^2)\right)$, which is the same to $\mathcal{O}(g)$. By contrast, each internal monomer belonging to a linear chain now brings the factor $\beta(1+g)$ instead of β. The number of such internal monomers is $\mathcal{N}_{ml} - 2\mathcal{N}_l$. The additional factor $1 + g(\mathcal{N}_{ml} - 2\mathcal{N}_l) + \mathcal{O}(g^2)$ should be introduced in the r.h.s. of eq. (1) as a result. Therefore

$$\partial \ln Z/\partial g\big|_{g=0} = \langle \mathcal{N}_{ml} - 2\mathcal{N}_l \rangle$$

A similar relation coming from the magnetic partition function is

$$\partial \ln Z_m/\partial g\big|_{g=0} = -\left\langle \partial H_m/\partial g \right\rangle_{g=0} = \frac{\mathcal{N}}{n-1}\left\langle \frac{n\varphi_1^2 - \varphi^2}{2/\beta + 2h\varphi_1 + \varphi^2} \right\rangle_{g=0}$$

As $\ln Z = \ln Z_m + \text{const}$, the above equations provide the total concentration of internal monomers of linear chains:

$$\phi_l - 2c_l = -\,\partial F_m/\partial g\big|_{g=0} = \left\langle \frac{\varphi_1^2 - \varphi_2^2}{2/\beta + 2h\varphi_1 + \varphi^2} \right\rangle \tag{18}$$

where φ_2 is a transverse component. The term $2c_l$ in the above equation can be neglected: $c_l \ll \phi_l$ for $N_m \gg 1$ as always assumed in what follows. On using eq. (17) we get concentration of units in the rings $\phi_r = \phi - \phi_l$:

$$\phi_r = n\left\langle \frac{\varphi_2^2}{2/\beta + 2h\varphi_1 + \varphi^2} \right\rangle \tag{19}$$

3.4. Fluctuation corrections and magnetic correlation functions

The fluctuation corrections to the mean-field results of the previous section can be found in a standard way by doing the quadratic expansion of $H_m[\varphi]$ near the minimum (near the mean-field solution $\varphi^*_{\alpha i} = m\delta_{\alpha 1}$) and using Fourier transforms of the fields:

$$\varphi_{\alpha,q} = \frac{1}{\sqrt{\mathcal{N}}}\sum_i \varphi_{\alpha i} e^{-\mathrm{i}q\cdot r_i}$$

so, for example,

$$H_0[\varphi] = \frac{1}{2}\sum_{q,\alpha} K^{-1}(q)\,|\varphi_{\alpha,q}|^2 \qquad (20)$$

with [6]

$$K(q) \equiv \sum_{\underline{s}} K_{\underline{s}} e^{\mathrm{i}\underline{q}\cdot\underline{s}}$$

Note that $K(0) = 1$ and $\int_q K(q)^2 = 1/z^*$, where $\int_q = \int \frac{\mathrm{d}^3 q}{(2\pi^3)} = \frac{1}{\mathcal{N}}\sum_q$, hence the function $K(q)$ is concentrated in a rather narrow region $q^3 \lesssim 1/z^*$. Thus we get

$$H_m[\varphi] \simeq H_m[\varphi^*] + \frac{1}{2}\sum_q J_1(q)\,|\delta\varphi_{1,q}|^2 + \frac{1}{2}\sum_{q,\alpha\neq 1} J_2(q)\,|\delta\varphi_{\alpha,q}|^2 \qquad (21)$$

where $\delta\varphi = \varphi - \varphi^*$, $J_1(q) = \frac{1}{K(q)} + 1 - \frac{2}{\beta}$, $J_2(q) = \frac{1}{K(q)} - 1$, $\beta > 1$, and $J_1(q) = J_2(q) = \frac{1}{K(q)} - \beta$, $\beta < 1$ (for $h = 0$). The polymer grand potential per site is

$$F = F_m(\beta) - F_m(0) = F_{mf} + F_{fl},$$

where F_{mf} is defined in eq. (7), and

$$F_{fl} \simeq \frac{1}{2}\left[I_1 + (n-1)I_2\right] \qquad (22)$$

is the main fluctuation correction with

$$I_1 = \int_q \ln\left(J_1(q)K(q)\right), \qquad I_2 = \int_q \ln\left(J_2(q)K(q)\right)$$

Both I_1 and I_2 are generally small in the mean-field regime: $I_1 \sim I_2 \sim 1/z^* \ll 1$.

Let us turn to correlation functions of the field φ. Above the transition, $\beta > 1$ ($\phi \simeq 1 - 1/\beta > 0$) we distinguish longitudinal and transverse fluctuations:

$$S_1(q) = \left\langle |\varphi_{1,q}|^2 \right\rangle, \qquad S_2(q) = \left\langle |\varphi_{2,q}|^2 \right\rangle$$

The mean-field correlation functions can be easily obtained using eq. (21):

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[6] We assume that the function $K_{\underline{s}}$ is nearly isotropic; therefore, $K(q)$ depends only on the magnitude of $\underline{q}$.

$$S_1(q) \simeq \frac{1}{J_1(q)} = \frac{K(q)}{1+(1-2/\beta)K(q)}, \quad S_2(q) \simeq \frac{1}{J_2(q)} = \frac{K(q)}{1-K(q)}, \quad \beta > 1 \tag{23}$$

In particular, $S_1(q) \simeq \frac{1}{2\phi+q^2a^2}$ for $\phi \ll 1$, since $1-K(q) \simeq a^2q^2$ for $q \ll 1/b$. Here $a^2 = \frac{b^2}{2d}$, $d=3$, and

$$b^2 = \sum_{\underline{s}} K_{\underline{s}} \underline{s}^2 \tag{24}$$

The real-space correlation functions, $G_1(r)$, $G_2(r)$, are defined by Fourier transforms of the above expressions. The longitudinal function

$$G_1(r) = \langle \varphi_1(0)\varphi_1(r) \rangle - \langle \varphi_1 \rangle^2 \tag{25}$$

(here $\varphi_1(r_i) \equiv \varphi_{1i}$). Hence

$$G_1(r) \simeq \frac{1}{4\pi a^2 r} e^{-r/\xi} \tag{26}$$

for $r \gg b$ and $1/z^{*2} \ll \phi \ll 1$, with the correlation length

$$\xi \simeq a/\sqrt{2\phi} \tag{27}$$

In a similar way, one finds that the transverse correlations are long-range:

$$G_2(r) = \langle \varphi_2(0)\varphi_2(r) \rangle \sim \frac{1}{r} \;, \quad r \gg b \tag{28}$$

Interestingly, for $\beta = 2$ (that is $\phi = 0.5$) $S_1(q) = K(q)$ hence $G_1(\underline{s}) = K_{\underline{s}} \lesssim 1/z^*$. This result illustrates the general feature: the fluctuations are weak in the mean-field regime, $G_{1,2}(r) \lesssim 1/z^*$.

So far we assumed that $h=0$. For small $h>0$ and $\beta>1$ we get

$$F_{mf} \simeq 1 - \frac{1}{\beta} - \ln\beta - h\sqrt{2(1-1/\beta)}, \quad h \ll 1$$

instead of F in eq. (7), and

$$S_2(q) \simeq \frac{K(q)}{1-(1-\delta)K(q)}, \quad \delta = h/\sqrt{2(1-1/\beta)}, \quad h \ll 1 \tag{29}$$

leading to

$$G_2(r) \simeq \frac{1}{4\pi a^2 r} e^{-r/\xi_m}, \quad r \gg b \tag{30}$$

with finite transverse correlation length

$$\xi_m \simeq a/\sqrt{\delta} \simeq a\sqrt{N_m}, \quad N_m \simeq \sqrt{2\phi}/h \tag{31}$$

Obviously, $K(q) \simeq 1$ for $q \ll 1/b$, so by virtue of eq. (6) $\varphi_q \simeq \sigma_q$ in this regime. Therefore, long-range parts of the spin correlation functions must nearly coincide with the analogous correlation functions of the field φ: $\langle \sigma_{\alpha i}\sigma_{\beta j} \rangle \simeq \langle \varphi_{\alpha i}\varphi_{\beta j} \rangle$ for $|r_{ij}| \gg b$.

We are now in a position to calculate the number of rings. On using eq. (1) we get $\langle \mathcal{N}_r \rangle = \frac{\partial \ln Z}{\partial \ln n}$, so the concentration of rings $c_r = \mathcal{N}_r/\mathcal{N} = -\frac{\partial F}{\partial \ln n}$. Further using eq. (22):

$$c_r \simeq -(n/2) I_2 \simeq -(n/2) \int_q \ln\left(1 - \tilde{\beta} K(q)\right)$$

where $\tilde{\beta} \simeq \beta$ for $\beta < 1$, $\tilde{\beta} \simeq 1 - \delta$ for $\beta > 1$ (here δ is defined in eq. (29), $h \ll 1$). The total concentration of all units in the rings is (see eq. (19))

$$\phi_r \simeq \frac{n}{2} \tilde{\beta} \left\langle \varphi_2^2 \right\rangle = \frac{n}{2} \tilde{\beta} \int_q S_2(q) \simeq \frac{n}{2} \tilde{\beta} \int_q \frac{K(q)}{1 - \tilde{\beta} K(q)} \tag{32}$$

Thus, both c_r and ϕ_r increase with β for $\beta < 1$, while $c_r, \phi_r \simeq \text{const} \sim 1/z^*$ for $\beta > 1$ and $h = 0$ in the mean-field regime.

3.5. Polymer correlation functions

The connection between polymer and magnetic correlation functions had been established long ago by De Gennes, Des Cloizeaux and others[45,46,33]. This analogy is particularly general and transparent for the model we consider.

Concentration of polymer units

Let us consider first the correlation function of concentration fluctuations. To assess it, we generalize eq. (5) introducing the field $\beta_i = e^{\mu_i}$ instead of the constant β. Then $Z_m[\mu] = \int e^{-H_m[\varphi,\mu]} \mathcal{D}[\varphi]$, giving the general thermodynamic relations like

$$\frac{\partial \ln Z_m}{\partial \mu_i} = \left\langle \frac{\partial H_m}{\partial \mu_i} \right\rangle, \quad \frac{\partial^2 \ln Z_m}{\partial \mu_i \partial \mu_j} = \left\langle \frac{\partial H_m}{\partial \mu_i} \frac{\partial H_m}{\partial \mu_j} \right\rangle - \left\langle \frac{\partial H_m}{\partial \mu_i} \right\rangle \left\langle \frac{\partial H_m}{\partial \mu_j} \right\rangle - \left\langle \frac{\partial^2 H_m}{\partial \mu_i \partial \mu_j} \right\rangle \tag{33}$$

A similar relation can be applied to the polymer partition function Z (eq. (1)), where $\beta^{\mathcal{N}_m}$ should be generalized as $e^{\sum_i \mu_i \phi_i}$ (here $\phi_i = 1$ if the site i is occupied by a monomer unit and $\phi_i = 0$ otherwise). Noting also that $\ln Z = \ln Z_m + \text{const}$ (see eq. (4)), one finds (for $h = 0$ and uniform system, $\beta_i = \beta$)

$$\phi = \langle \phi_i \rangle = \left\langle \frac{\varphi_i^2}{2/\beta + \varphi_i^2} \right\rangle, \quad \langle \phi_i \phi_j \rangle = \left\langle \frac{\varphi_i^2}{2/\beta + \varphi_i^2} \frac{\varphi_j^2}{2/\beta + \varphi_j^2} \right\rangle$$

where $\varphi_i^2 \equiv \varphi_{\alpha i} \varphi_{\alpha i}$. The correlation function of concentration

$$G_p(\underline{r}_i - \underline{r}_j) = \langle \phi_i \phi_j \rangle - \langle \phi_i \rangle \langle \phi_j \rangle \tag{34}$$

can be thus written as:

$$G_p(r) = \left\langle \frac{\varphi(0)^2}{2/\beta + \varphi(0)^2} \frac{\varphi(\underline{r})^2}{2/\beta + \varphi(\underline{r})^2} \right\rangle - \phi^2, \quad r > 0 \tag{35}$$

where $\varphi(\underline{r}_i) \equiv \varphi_i$. Obviously, $G_p(0) = \phi(1 - \phi)$ in the general case. Taking into account that φ-fluctuations are weak, we can write $\frac{\varphi(r)^2}{2/\beta + \varphi(r)^2} \simeq \phi + \frac{m}{\beta} \delta\varphi_1(r)$ with $\delta\varphi_1(r) = \varphi_1(r) - m$, $m = \langle \varphi_1 \rangle$. Hence

$$G_p(r) \simeq 2\phi(1 - \phi)^2 G_1(r), \quad r \neq 0 \tag{36}$$

or

$$G_p(r) \simeq \frac{2\phi(1-\phi)^2}{4\pi a^2 r} e^{-r/\xi} \tag{37}$$

for $r \gg b$ (see eq. (26)).

The polymer structure factor

$$S_p(q) = \int G_p(r) e^{-\mathrm{i}q\cdot r} \mathrm{d}^3 r$$

is then given by

$$S_p(q) \simeq 2\phi(1-\phi)^2 S_1(q) + \phi(1-\phi)$$

where $S_1(q)$ is defined in eq. (23) (here we also use that $G_1(0) \sim 1/z^* \ll 1$), i.e.

$$S_p(q) \simeq \phi(1-\phi) \frac{1+K(q)}{1+(2\phi-1)K(q)} \tag{38}$$

Note that $S_p(0) \simeq 1-\phi$ obeys the general relation $S_p(0) = 1/v^*$, where $v^* = \partial^2 f_p/\partial\phi^2$ (see eq. (10)). Moreover, $S_p(q)$ satisfies the basic RPA relation[45,47]

$$1/S_p(q) = 1/\left[\phi F(q)\right] + v^*,$$

where

$$F(q) = \frac{1+K(q)}{1-K(q)}$$

is the formfactor of the ideal infinite chain (recall that for $h=0$ all linear chains are infinite, and their statistics is nearly ideal in the mean-field regime).

Correlation functions of chain ends.

Two correlation functions are associated with the chain ends: $G_e(\underline{r})$ is the excess probability that both sites 0 and $\underline{r}$ are occupied by chain ends,

$$G_e(\underline{r}) = \langle c_e(0) c_e(\underline{r}) \rangle - c_e^2 \tag{39}$$

where $c_e(r)$ is the local concentration of chain ends, and $c_e = 2c_l$ is its mean value. Demanding in addition that the two ends belong to the same chain, we get the end-to-end correlation function

$$F_e(\underline{r}) = c_e P(\underline{r}) \tag{40}$$

where $P(\underline{r})$ is the probability density for the end-to-end vector $\underline{r}$ of a linear chain.

The function $G_e(r)$ (for $r > 0$) can be defined in magnetic terms considering slightly inhomogeneous magnetic field $h \to h_i$. Thus

$$G_e(r) = h^2 \left\langle \frac{2\varphi_1(0)}{2/\beta + 2h\varphi_1(0) + \varphi(0)^2} \frac{2\varphi_1(r)}{2/\beta + 2h\varphi_1(r) + \varphi(r)^2} \right\rangle - c_e^2 \tag{41}$$

To get the second correlation function, $F_e(r)$, we consider magnetic field with slightly inhomogeneous direction replacing $h\varphi_{1i}$ in eq. (5) with $h\varphi_{1i} + h_{2i}\varphi_{2i}$. The polymer partition function (see eq. (1)) changes as a result: each linear chain with ends at sites i and j brings an additional statistical factor $1 + h_{2i}h_{2j}/h^2$. On using relations like eqs. (33) and setting $h_2 \to 0$, we find for $r > 0$

$$F_e(r) = h^2 \left\langle \frac{2\varphi_2(0)}{2/\beta + 2h\varphi_1(0) + \varphi(0)^2} \frac{2\varphi_2(r)}{2/\beta + 2h\varphi_1(r) + \varphi(r)^2} \right\rangle$$

The above results can be significantly simplified for $h \ll 1$ and $z^* \gg 1$:

$$G_e(r) \simeq A^2 G_1(r), \quad F_e(r) \simeq A^2 G_2(r), \quad c_e \simeq Am \tag{42}$$

where the magnetic functions G_1, G_2 are defined in eqs. (25), (28), and

$$A = \beta h / \left(1 + \beta m^2/2\right) \simeq \begin{cases} h & , \ \beta > 1, \\ \beta h & , \ \beta < 1 \end{cases} \tag{43}$$

Here we take into account that $m \simeq \sqrt{2\phi_l}$, $\phi_l \simeq 1 - 1/\beta$ in the mean-field regime ($\phi_l \gg 1/z^{*2}$, see eq. (11)), and that $m = 0$ below the transition, $\beta < \beta^* \simeq 1$. Note that eqs. (42), (43) are valid for any β including the critical transition region around $\beta \simeq 1$. Thus (see eq. (30))

$$F_e(r) \simeq h^2 G_2(r) \simeq \frac{h^2}{4\pi a^2 r} e^{-r/\xi_m} \quad , \quad r \gg b \tag{44}$$

where ξ_m is defined in eq. (31). Alternatively, the same function can be obtained as $F_e(r) = c_e P(r)$. By virtue of the Flory distribution for the chain length N (see eq. (15)) and the Gaussian statistics for the end-to-end vector $\underline{r}$ of an N-chain having the distribution[50]

$$P(r, N) = \left(4\pi N a^2\right)^{-3/2} \exp\left(-\frac{r^2}{4Na^2}\right) \tag{45}$$

we get

$$P(r) \simeq \int_0^\infty \delta e^{-N\delta} P(r, N) \mathrm{d}N = \frac{\delta}{4\pi a^2 r} e^{-r/\xi_m}$$

leading to $F_e(r) = c_e P(r)$ which coincides with eq. (44). Obviously, the terminal length ξ_m there has the meaning of the typical chain size: $\xi_m = a\sqrt{N_m}$.

4. Long-range concentration fluctuations

In this section we show that concentration fluctuations in living polymer systems are generally characterized by a long length-scale $\gg \xi$. This property is associated with the long-range character of the magnetic correlation function $G_2(r)$ as was revealed for the model with $n = 0$.[31,32] For simplicity, we consider here the mean-field regime, eq. (11), although this condition is unimportant and is lifted later.

4.1. Correlation function $G_p(r)$

Let us start with $h \to 0$ ($N_m \to \infty$). For $z^* \gg 1$ the function $G_p(r)$ is defined in eq. (35). It is approximated in eq. (36) providing the mean-field result, eq. (37), with correlation length $\xi \sim a/\sqrt{\phi}$. Note that eq. (36) was derived neglecting transverse fluctuations, $\varphi_2(r)$. Indeed, it seems that these fluctuations do not affect much $\varphi(r)^2$. It is important, however, that the transverse correlation function is singular at large length-scales, $S_2(q) \propto 1/q^2$ for $q \lesssim 1/b$, hence its effect generates an important long-range correlation term $G_{lr}(\mathrm{r})$, as shown below. To account for the transverse effect directly one would have to calculate many higher order correlation functions involving transverse and longitudinal fields, φ_2, φ_1. To avoid this, it is better to change variables as demonstrated below for $n = 2$ (the generalization of this approach to any n is straightforward).

The magnetic Hamiltonian H_m is defined in eqs. (5), (20). As we are interested in the long-range effects, we can assume $q \ll 1/b$, so $1/K(q) \simeq 1 + q^2a^2$. Thus, we get

$$H_m \simeq \frac{1}{2}\int \left[\varphi^2 + a^2\left(\nabla\varphi\right)^2 - 2\ln(1+\beta\varphi^2/2)\right] \mathrm{d}^3r \tag{46}$$

where $\varphi = \varphi(r)$. Let us define new variables: $u \equiv \varphi^2/2$ and θ, the polar angle in the φ_1, φ_2 plane ($\tan\theta = \varphi_2/\varphi_1$). The Jacobian of the transformation is $\partial(u,\theta)/\partial(\varphi_1,\varphi_2) = 1$. The Hamiltonian then becomes:

$$H_m = \int \left[f_m(u) + \frac{a^2}{4}\frac{\left(\nabla u\right)^2}{u} + a^2 u\left(\nabla\theta\right)^2\right] \mathrm{d}^3r$$

where $f_m(u) = u - \ln(1+\beta u)$. The minimum of f_m corresponds to $u = u^* = 1 - \frac{1}{\beta} \simeq \phi$, $\langle u\rangle \simeq u^*$. Expanding H_m in $\eta \equiv u - u^*$ we get (omitting constant term) $H_m = H_2 + H_3$, where

$$H_2 = \int \left[\frac{\eta^2}{2} + \frac{a^2}{4\phi}\left(\nabla\eta\right)^2 + a^2\phi\left(\nabla\theta\right)^2\right] \mathrm{d}^3r$$

$$= \frac{1}{2}\sum_q \left\{\left|\eta_q\right|^2\left[1 + \frac{a^2q^2}{2\phi}\right] + 2\phi a^2q^2\left|\theta_q\right|^2\right\}$$

is the quadratic term, and H_3 includes the cubic and higher order terms:

$$H_3 = \int \left[-\eta^3/3 + a^2\eta\left(\nabla\theta\right)^2 - \frac{a^2}{4\phi^2}\eta\left(\nabla\eta\right)^2 + ...\right] \mathrm{d}^3r \tag{47}$$

Using eq. (35) we get

$$G_p(r) = \left\langle \frac{1}{1+\beta u(0)}\frac{1}{1+\beta u(r)}\right\rangle_c \simeq (1-\phi)^2\left\langle\eta(0)\eta(r)\right\rangle_c, \quad r \neq 0 \tag{48}$$

where index ‘c’ means cumulant average. To calculate $G_p(r)$ it suffice to find $S_\eta(q) \equiv \left\langle\left|\eta_q\right|^2\right\rangle_c$, where η_q is the Fourier transform of $\eta(r)$. Using the quadratic approximation, $H \simeq H_2$, we get $\left\langle |\eta_q|^2 \right\rangle_{H2} = \frac{1}{1+a^2q^2/(2\phi)}$ and recover the mean-field result for G_p:

$$G_p(r) \simeq G_{mf}(r) = (1-\phi)^2 \int_q \left\langle |\eta_q|^2 \right\rangle_{H2} e^{\mathrm{i}q\cdot r} = (1-\phi)^2 \frac{2\phi}{4\pi a^2} \frac{1}{r} e^{-r/\xi} \tag{49}$$

coinciding with eq. (37) (here $\xi = a/\sqrt{2\phi}$). Taking into account the effect of H_3 leads to

$$S_\eta(q) = \left\langle |\eta_q|^2 e^{-H_3} \right\rangle_{H2} / \left\langle e^{-H_3} \right\rangle_{H2} = \left\langle |\eta_q|^2 \right\rangle_{H2} + \Delta S_\eta(q)$$

An analysis shows that the dominant long-range contributions to the correction term $\Delta S_\eta(q)$ are generated by the second term in H_3, eq. (47):

$$\Delta S_\eta(q) \simeq \frac{2a^4}{V} \sum_{q'} \left(\left\langle |\eta_q|^2 \right\rangle_{H2} \right)^2 \left\langle (\nabla_\omega \theta)_{q'} (\nabla_v \theta)_{-q'} \right\rangle_{H2} \left\langle (\nabla_\omega \theta)_{q''} (\nabla_v \theta)_{-q''} \right\rangle_{H2} \tag{50}$$

where $V = \mathcal{N}$ is the total volume of the system, and the summations over $\omega, v = 1..d$ (d is the space dimension, $d = 3$ was assumed before) and over q' under the condition $\underline{q}' + \underline{q}'' = \underline{q}$ are assumed. As we are interested in the long-range effect, $1/q \gg \xi$, the factor $\left\langle |\eta_q|^2 \right\rangle_{H2}$ in this sum can be approximated as 1. Hence, the sum can be rewritten as

$$\Delta S_\eta(q) \simeq \frac{2a^4}{V} \sum_{q',\omega,v} q'_\omega q'_v q''_\omega q''_v S_{2\theta}(q') S_{2\theta}(q''), \tag{51}$$

where $\underline{q}' + \underline{q}'' = \underline{q}$, and

$$S_{2\theta}(q) = \left\langle |\theta_q|^2 \right\rangle_{H2} = \frac{1}{2a^2\phi q^2}$$

The corresponding real-space correlation function is

$$G_{2\theta}(r) = \langle \theta(0)\theta(r) \rangle = \left[2(d-2) S_d a^2 \phi \right]^{-1} r^{2-d}$$

where $S_d = 2\pi^{d/2}/\Gamma(d/2)$ is the area of unit sphere in the d-dimensional space.

The concentration correlation function is thus

$$G_p(r) = G_{mf}(r) + G_{lr}(r) \tag{52}$$

where the short-range contribution $G_{mf}(r)$ is defined in eq. (49), and

$$G_{lr}(r) = (1-\phi)^2 \int_q \Delta S_\eta(q) e^{\mathrm{i}q\cdot r}$$

Using eq. (51) gives

$$G_{lr}(r) \simeq 2(1-\phi)^2 a^4 \sum_{\omega,v} \nabla_\omega \nabla_v G_{2\theta}(r) \nabla_\omega \nabla_v G_{2\theta}(r) \tag{53}$$

Thus, the long-range part of $G_p(r)$ is

$$G_{lr}(r) \simeq C_d \frac{1}{v^{*2}\phi^2} r^{-2d} \tag{54}$$

where $C_d = 0.5d(d-1)/S_d^2$ and $v^* = 1/(1-\phi)$. This result can be further generalized for any n which can be treated in a similar way (the general substitution involves $u = \varphi^n/n$ and $n-1$ angular variables). The result coincides with eq. (54), but with additional factor $n-1$:

$$G_{lr}(r) \simeq C_d \frac{n-1}{(v^*\phi)^2} r^{-2d} \tag{55}$$

Eq. (55) is valid generally, and not only in the mean-field regime, if we replace $v^*\phi$ by $\varkappa \equiv \phi_l \partial\mu/\partial\phi_l$, where $\mu = \ln\beta$ is the monomer chemical potential, and ϕ_l is volume concentration of linear chains ($\phi_l = \phi$ in the mean-field approximation, hence $v^*\phi = \phi_l\partial\mu/\partial\phi_l$):

$$G_{lr}(r) \simeq C_d(n-1)\varkappa^{-2} r^{-2d} \tag{56}$$

Note that $\varkappa \simeq \phi_l$ for $\phi_l \ll 1$. For $d = 3$, $h = 0$ we thus have $G_{lr}(r) \simeq \frac{3(n-1)}{(4\pi\varkappa)^2} r^{-6}$. Eq. (56) is in agreement with the results of refs.[31,32], where the case $n = 0$ (no polymer rings) was considered.

For $h > 0$ the correlation function $G_{2\theta}(r)$ decays exponentially at $r \gtrsim \xi_m$. Its Fourier image $S_{2\theta}(q) \propto S_2(q) \propto 1/(q^2 + \xi_m^{-2})$. The exact result for $d = 3$ is simple (cf. eqs. (30), (C12) noting that $G_{2\theta}(r) \propto G_2(r)$):

$$G_{2\theta}(r) \propto \frac{1}{4\pi r} e^{-r/\xi_m}$$

where

$$\xi_m = a^* \sqrt{N_m} \tag{57}$$

is the terminal coil size ($\sqrt{6}a^*$ is the polymer chain statistical segment, which is renormalized by fluctuations in the general case; $a^* \simeq a$ in the mean-field regime). Then, on using eq. (53) we get for $d = 3$, $h > 0$, $r \gg \xi$:

$$G_{lr}(r) \simeq \frac{3(n-1)}{(4\pi\varkappa)^2} r^{-6} e^{-2r/\xi_m} \left\{ 1 + 2\frac{r}{\xi_m} + \frac{5}{3}\frac{r^2}{\xi_m^2} + \frac{2}{3}\frac{r^3}{\xi_m^3} + \frac{1}{6}\frac{r^4}{\xi_m^4} \right\} \tag{58}$$

For arbitrary d, h, the long-range part of the correlation function of polymer concentration, $G_{lr}(r)$, is defined in eq. (56) for $\xi \ll r \ll \xi_m$, and

$$G_{lr}(r) \sim (n-1)\varkappa^{-2} r^{-2d} e^{-2r/\xi_m}, \quad r \gg \xi \tag{59}$$

Thus, we considered the long-range effect of transverse modes exhibited in the polymer concentration correlation function $G_p(r)$ and found that the genuine (terminal) decay length for concentration correlations is ξ_m if $n \neq 1$.

For $n > 0$ the correlation function $G_p(r)$ has to be modified also at short r, where eq. (49) becomes invalid. Formally, within the magnetic model, this breakdown is related to strong fluctuations of φ in this regime: the typical amplitude, $\delta\varphi$, at the length-scale r is $\delta\varphi^r \sim \sqrt{G_1(r)}$ with $G_1(r) \sim 1/\left(a^2 r^{d-2}\right)$. Hence $\delta\phi^r$ becomes larger than $m \sim \sqrt{\phi_l}$ for $r \lesssim \tilde{r}$, where $\tilde{r}^{d-2} \sim 1/(\phi_l a^2)$. The modified short-range contribution, $G_{mf}(r)$ (cf. eq. (52)) can be obtained directly based on the quadratic part of the magnetic Hamiltonian, eq. (46) (cf. eq. (21)). Eq. (35) gives

$$G_p(r) \simeq \frac{(1-\phi)^2}{4} \left\langle \left(\varphi(0)^2 - m^2\right) \left(\varphi(r)^2 - m^2\right) \right\rangle$$

Obviously $\varphi(r)^2 - m^2 = 2m\delta\varphi_1(r) + (\delta\varphi(r))^2$. Taking into account that fluctuations, $\delta\varphi(r)$, are nearly Gaussian at $r \lesssim \xi$, we find

$$G_{mf}(r) \simeq 2\phi_l G_1(r) + G_1(r)^2/2 + (n-1)G_2(r)^2/2$$

Here we omitted the factor $(1-\phi)^2$ assuming that $\phi \ll 1$. Obviously, the first term in the above equation agrees with eq. (49). For $r \ll \xi$ the two magnetic functions nearly coincide:

$$G_1(r) \simeq G_2(r) \simeq A_d / \left(a^2 r^{d-2}\right)$$

where $A_d = \Gamma(d/2-1)\pi^{-d/2}/4$. Hence

$$G_{mf}(r) \simeq 2\phi_l G_1(r) + \frac{n}{2} G_1(r)^2, \quad r \ll \xi \tag{60}$$

As shown in Appendix D, the new term (the second term proportional to n) is due to the effect of rings. Hence, for $n > 0$, $G_p(r) \propto r^{4-2d}$ for $r \lesssim \tilde{r} \sim (\phi_l a^2)^{1/(2-d)}$ (the ring dominance regime) and $G_p \propto r^{2-d}$ for $\tilde{r} \lesssim r \lesssim \xi$ (the linear chain dominance regime). [7] In particular, for $d = 3$ eqs. (60), (49) give:

$$G_{mf}(r) \simeq \left(\frac{2\phi_l}{4\pi a^2 r} + \frac{n}{2} \left(\frac{1}{4\pi a^2 r} \right)^2 \right) e^{-r/\xi}, \quad r \lesssim \xi \tag{61}$$

The total correlation function is defined in eq. (52) as a sum of the short-range (eqs. (60), (61)), and the long-range (eqs. (58), (59)) contributions.

4.2. Polymer-induced interaction

Now we briefly consider interaction between two solid surfaces in a living polymer solution. Within the polymer-magnetic analogy, the long-range interaction at the separation $D \gg \xi$ is generated by the soft transverse modes of spin fluctuations.[31,32] The separation D between the surfaces defines the lowest $q = \pi/D$ for these transverse fluctuations. The long-range interaction energy is essentially proportional to the number of soft modes, that is, to $n-1$. As a result we get the following polymer-induced interaction energy per unit area (we consider the case $h = 0$ corresponding to infinite linear chains):[31,32]

$$W = \text{const} + (1-n)B_d/D^{d-1}, \qquad D \gg \xi$$

where $B_d = \Gamma(d/2)\zeta(d)/(2\sqrt{\pi})^d$, $B_3 = \zeta(3)/(16\pi)$. In the case of directional polymers ($n = 2$) in 3d space we thus predict a long-range attraction: $W_{lr} \sim -1/D^2$.

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[7] Note that $\tilde{r}$ is comparable with the size of the concentration blob for linear chains: such blobs nearly tightly fill the whole volume, so the linear chains form a sort of polymer melt of the blobs.

5. The critical fluctuation region

5.1. The basic scaling laws, chain-length distributions and correlation functions of chain ends

Both magnetic and polymer systems show critical behavior near the transition point $\beta = \beta^*$. The critical polymer exponents were identified based on the general polymer-magnetic relations (cf. eqs. (13), (17), (18), (35), (42)) following the basic ideas introduced in refs.[20]. In this section we reconsider the critical properties of living polymers focusing, where appropriate, on the polymer aspect of the problem. The relevant properties of magnetic systems are summarized in the Appendix B.

We start with the case $h = 0$ (infinitely long linear chains). The living polymerization then occurs as a phase transition at $\beta = \beta^*$ (recall that $\beta^* \simeq 1$ for $z^* \gg 1$), so $\tau = \ln(\beta/\beta^*)$ is the relevant parameter corresponding to the reduced temperature in magnetic systems (see Appendix B). The total concentration of monomer units is (cf. eqs. (8), (17))

$$\phi = \left\langle \frac{\varphi^2}{2/\beta + \varphi^2} \right\rangle = -\frac{\partial F}{\partial \tau} \tag{62}$$

On using eqs. (B8), (B6):

$$\phi = \phi^* + \text{const } |\tau|^{d\nu - 1} \operatorname{sgn}(\tau) \tag{63}$$

where ϕ^* corresponds to the transition point. The osmotic compressibility $\chi_p = \partial\phi/\partial\tau = S_p(0)$ is analogous to heat capacity for magnetic systems, and its singular part is (cf. eq. (B7))

$$\chi_p \sim |\tau|^{d\nu - 2} \equiv |\tau|^{-\alpha} \tag{64}$$

Note that α is positive for $n = 1$, but it is slightly negative for $n = 2$: a weak critical behavior of χ_p is thus predicted for directional polymers, $n = 2$.

Now, let us turn to the living polymer system exactly at the transition point $h = 0$, $\tau = 0$. There are only finite rings of different sizes in the system. To establish their size distribution let us consider the statistics of an added tracer linear chain of N units. One can think about effective interactions between its segments defining the statistics. These interactions are partially screened by the presence of the rings, hence the tracer chain swelling can be weaker than for a self-avoiding chain.[20] A distinct scaling law for the tracer chain size, $R(N)$, is thus expected:

$$R(N) \sim N^{\nu_p} \tag{65}$$

where ν_p may be different from the classical Flory exponent ($b \sim 1$ is assumed here for simplicity).

The (grand) partition function of the tracer chain (its statistical weight) $Z_l(N)$ can be also written in analogy with the self-avoiding polymers:

$$Z_l(N) \sim Z_1^N N^{\gamma_p - 1} \tag{66}$$

where γ_p in another unknown exponent, and Z_1 is the statistical weight per unit including the factor β involved in eq. (1). It is easy to argue that $Z_1 = 1$ at

$\tau = 0$. In fact, with $Z_1 > 1$ very long linear chain would gain exponentially large statistical weight which is impossible. Therefore $Z_1 \leq 1$. On the other hand, $Z_1 < 1$ means that the statistical weight of very long chains is exponentially small even for certain $\tau > 0$, so the polymerization transition could not occur at $\tau = 0$.

The size of the closed tracer chain with zero end-to-end distance is still defined by eq. (65), while its statistical weight is related to $R(N)$:[45]

$$Z_r(N) \sim Z_1^N R(N)^{-d} \sim N^{-\nu_p d}, \quad \tau = 0$$

The concentration $c_r(N)$ of N-rings is proportional to $Z_r(N)$:

$$c_r(N) = \frac{n}{2} Z_r(N)/N \sim N^{-\nu_p d - 1}, \quad \tau = 0 \tag{67}$$

where the factor $1/N$ accounts for equivalence of all units in a ring, the factor $n/2$ accounts for 2 directions along the ring (which are equivalent for $n = 1$, but not for $n = 2$ corresponding to directional polymers). Eq. (67) defines the size distribution of the rings at the critical point.

For $h > 0$ some linear chains must be present in the system. Their fraction is very small for $\tau = 0$ and $h \to 0$. In this regime, the partition function of a linear chain is simply proportional to $Z_l(N)$ for the tracer chain. The concentration $c_l(N)$ of linear chains with exactly N units therefore is:

$$c_l(N) = h^2 Z_l(N) \sim h^2 N^{\gamma_p - 1} e^{-\delta N} \tag{68}$$

where h^2 is the statistical weight due to the two chain ends, and $e^{-\delta} = Z_1$, $\delta \to 0$ for $h \to 0$.

It remains to find the exponents ν_p and γ_p. To this end we turn to the regime $\tau > 0$, $h \to 0$, where some infinite linear chains are formed, their volume concentration is $\phi_l > 0$. Obviously $Z_1 = 1$ in this regime like for $\tau = 0$. Eqs. (65), (66) remain valid for short enough tracer chains ($N \ll N^*$) that do not interact with the linear chain component. The latter condition can be clarified using the blob concept[45]. Consider each linear chain as a sequence of chain segments of N units each (N-blobs). The size of each blob is still defined by eq. (65). Therefore, the fraction of the volume occupied by the blobs is $\phi_b = (\phi_l/N)R(N)^d \sim \phi_l N^{\nu_p d - 1}$. The tracer chain nearly does not interact with linear chains if $\phi_b \ll 1$. Hence, the condition $N \ll N^*$ comes from $\phi_b \ll 1$, that is

$$N^* \sim \phi_l^{-1/(\nu_p d - 1)} \tag{69}$$

For $N \gg N^*$ the N-segments of linear chains are strongly overlapping, so their statistics must change: in fact, as verified below (see eq. (78)), the chains are nearly Gaussian[45] at such long length scales (beyond $R(N^*) \sim (N^*)^{\nu_p}$). According to the self-similarity hypothesis (which is well-established for magnetic systems[49]), the system near the critical point is characterized by a single essential length ξ (for $h = 0$, as long as we are interested in length-scales much exceeding the atomic size). Therefore, $R(N^*)$ must be identified with this correlation length: $R(N^*) \sim \xi \sim \tau^{-\nu}$ (cf. eq. (B14)),

$$(N^*)^{\nu_p} \sim \tau^{-\nu} \tag{70}$$

The fraction ϕ_l can be found using eqs. (B11), (18):

$$\phi_l \sim \tau^{\nu d - \phi_g} \tag{71}$$

Eqs. (69), (70), (71) together lead to the following relation between the exponents: $(\nu/\nu_p)(\nu_p d - 1) = \nu d - \phi_g$, hence

$$\nu_p = \nu/\phi_g, \quad N^* \sim \tau^{-\phi_g}$$

in full agreement with the results obtained in refs.[20]. The numerical values of ν_p for $d = 3$ are shown in Table 1.

To find another polymer exponent, γ_p, let us consider the end-correlation function $F_e(r)$ for $h \to 0$. It is related to the magnetic function $G_2(r)$ by eq. (42):

$$F_e(r) \sim h^2 G_2(r)$$

which gives in the scaling regime (see eq. (B17)):

$$F_e(r) \propto r^{\gamma/\nu - d}, \quad r \ll \xi \tag{72}$$

On the other hand, $F_e(r)$ for $r > 0$ is related to the length distribution function $c_l(N)$ of linear chains (cf. eq. (40)):

$$F_e(r) = 2 \int c_l(N) p(r, N) \mathrm{d}N \tag{73}$$

where $p(r, N)$ is the distribution function of the end-to-end vector. The above integral is dominated by $N \sim N_r$, where $R(N_r) \sim r$: $p(r, N)$ is exponentially small for short N with $R(N) \ll r$, while for large $N \gg N_r$ the integrand decreases sufficiently fast: $c_l(N)p(r, N) \propto Z_r(N) \sim N^{-\nu_p d}$, $\nu_p d > 1$. Obviously, $p(r, N) \sim 1/r^d$ for $N \sim N_r$. Therefore, $F_e(r) \sim c_l(N_r)N_r/r^d \propto N_r^{\gamma_p}/r^d \sim r^{\gamma_p/\nu_p - d}$ (note that $\delta \to 0$ for $h \to 0$). Comparing it with eq. (72) we find $\gamma_p/\nu_p = \gamma/\nu$, hence

$$\gamma_p = \gamma/\phi_g$$

The numerical values of γ_p are also given in Table 1.

We are now in a position to consider the chain length distribution $c_l(N)$ and correlations of chain ends in more detail for $0 < \tau \ll 1$, $h \to 0$. Eq. (68) remains valid for short enough chains, $N \lesssim N^*$, that virtually do not overlap (do not interact) with the surrounding linear chains. For $N \gg N^*$ the excluded-volume interactions are screened, so the mean-field result (cf. eq. (15)) is applicable: $c_l(N) \propto e^{-\delta N}$ (this exponential distribution is verified below, see eq. (77)). Thus $c_l(N) = h^2 Z_l(N)$ with

$$Z_l(N) \sim \begin{cases} N^{\gamma_p - 1} e^{-N\delta} & , \ N \lesssim N^* \\ (N^*)^{\gamma_p - 1}\, e^{-N\delta} & , \ N \gtrsim N^* \end{cases} \tag{74}$$

Eq. (74) allows to calculate the number concentration c_l of linear chains and their volume fraction ϕ_l:

$$c_l = \int c_l(N) \mathrm{d}N = h^2 \int Z_l(N) \mathrm{d}N, \quad \phi_l = \int c_l(N) N \mathrm{d}N \tag{75}$$

We still consider the regime of low h, where $N_m = 1/\delta \gg N^*$. Therefore, only the second line of eq. (74) is relevant for c_l, ϕ_l, and we get

$$c_l \sim h^2 \left(N^*\right)^{\gamma_p - 1} N_m, \quad \phi_l \sim h^2 \left(N^*\right)^{\gamma_p - 1} N_m^2 \tag{76}$$

On the other hand, $c_l \sim hm \sim h\tau^{(d\nu-\gamma)/2}$ (cf. eqs. (16), (B3)) and ϕ_l is defined in eq. (71). Thus, eqs. (76) provide two ways to find N_m (based on c_l and ϕ_l). The results are identical:

$$N_m \sim h^{-1}\tau^{(\nu d+\gamma)/2-\phi_g} \tag{77}$$

This agreement supports the validity of the exponential distribution of chain length for $N \gg N^*$; the second line in eq. (74) is thus verified.

Let us return to the correlation function for the ends of the same chain (cf. eq. (72)). For small h it is defined in eqs. (42), (B17):

$$F_e(r) \sim h^2 G_2(r) \sim \begin{cases} h^2 r^{\gamma/\nu-1} & , \ r \ll \xi \\ h^2 \xi^{\gamma/\nu-d}(r/\xi)^{2-d} e^{-r/\xi_m} & , \ r \gg \xi \end{cases} \tag{78}$$

where $\xi_m \sim h^{-0.5}\tau^{(d\nu+\gamma)/4-\nu}$ (cf. eq. (B16)). Obviously, ξ_m must be associated with the terminal size $R(N_m)$ of linear chains. Recalling that $R(N^*) \sim \xi$ and assuming a power law, $R \propto N^x$, in the range $N^* < N < N_m$, we find $x = 0.5$ pointing again to the Gaussian chain statistics in this regime. Thus, the typical end-to-end size of a linear N-chain is (cf. eq. (65))

$$R(N) \sim \begin{cases} N^{\nu_p} & , \ N \ll N^* \\ \left(N^*\right)^{\nu_p} \left(N/N^*\right)^{0.5} & , \ N \gg N^* \end{cases}$$

More precisely, the second line can be written as

$$R(N) \simeq b^* \sqrt{N}, \quad N \gg N^*$$

where $b^* = \sqrt{2d}a^*$ is the effective statistical segment,

$$a^* \sim \xi^{1-\phi_g/(2\nu)} \tag{79}$$

Moreover, the second line in eq. (78) can be made quantitative based on the Gaussian statistics of long chains, $N \gg N^*$. To this end we use eq. (73) noting that

$$c_l(N) \simeq \frac{\phi_l}{N_m^2} e^{-N/N_m}, \qquad N \gg N^*$$

(cf. eq. (74)) and that $p(r, N)$ is Gaussian (cf. eq. (45)):

$$p(r, N) \simeq \left(4\pi N a^{*2}\right)^{-d/2} \exp\left(-\frac{r^2}{4Na^{*2}}\right) \tag{80}$$

yielding an asymptotically exact result:

$$F_e(r) \simeq \frac{2\phi_l}{N_m^2 a^{*2}} \frac{1}{4\pi r} e^{-r/\xi_m}, \quad d = 3, \quad r \gg \xi \tag{81}$$

where $\xi_m^2 = N_m a^{*2}$. The above equation agrees with eq. (C11) (obtained in Appendix C using the magnetic analogy) and with the second line of eq. (78).

Let us now turn to the correlation function for ends of *different* chains, $\tilde{G}_e(r)$, defined as the probability that both sites 0 and $\underline{r}$ are occupied by end units of two chains. Obviously $\tilde{G}_e(\infty) = c_e^2$, and (cf. eq. (39))

$$g_e(r) \equiv \tilde{G}_e(r)/\tilde{G}_e(\infty) = [G_e(r) - F_e(r)]/c_e^2 + 1$$

The function $g_e(r)$ characterizes the effective interaction between the chain ends. Using eq. (42) we get

$$g_e(r) - 1 \sim [G_1(r) - G_2(r)]/m^2 \tag{82}$$

where $m = \langle \varphi_1 \rangle$. Applying eqs. (B15), (B17) we then get [8]

$$g_e(r) - 1 \sim (r/\xi)^{2-d}\left(e^{-r/\xi} - 1\right), \quad r \gtrsim \xi \tag{83}$$

This result shows that $g_e(r)$ decreases down to $g_e \sim 0.5$ at $r \sim \xi$, pointing to a significant effective repulsion of chain ends at distances $r \lesssim \xi$. In other words, the blobs of size ξ (concentration blobs of N^* units) significantly repel each other. This conclusion is in line with the basic idea[45] of just marginal penetration of concentration blobs. As follows from eq. (83),

$$g_e(r) \simeq 1 - \text{const}\,(r/\xi)^{2-d}, \quad r \gg \xi \tag{84}$$

On the other hand, for $r \ll \xi$ we get nothing from eq. (82) as the leading terms in G_1 and G_2 cancel each other in this regime. Instead, the dependence $g_e(r)$ for short r, $1 \ll r \ll \xi$, can be deduced by a standard scaling argument, assuming a power-law, $g_e(r) \propto r^x$, in this regime. It is useful to note that the case $r \sim 1$ means that 2 chains (N_1 and N_2) meet end-to-end effectively forming a longer chain ($N_1 + N_2$). Therefore

$$g_e \sim Z_l(N_1 + N_2)/\left[Z_l(N_1)Z_l(N_2)\right], \quad r \sim 1$$

Taking into account that the chains are typically long, $N \gg N^*$, and using eq. (74) we find $g_e(1) \sim (N^*)^{1-\gamma_p} \sim \xi^{(1-\gamma_p)/\nu_p}$. The scaling law is then obtained on recalling that $g_e(\xi) \sim 0.5$:

$$g_e(r) \sim (r/\xi)^{(\gamma_p - 1)/\nu_p}, \quad r \ll \xi \tag{85}$$

Eq. (84) can be understood in a simple way using the ansatz that the linear chains follow the Gaussian statistics at large length-scales, $r \gg \xi$.[45]. Suppose the site at the origin is occupied by an end of a long chain (which is considered as labelled). By virtue of the Gaussian statistics, the number of labelled units in a region V_r of radius $r \gg \xi$ is $g \sim N^*(r/\xi)^2$. As the polymer density is constant at $r \gg \xi$, the total number $\mathfrak{N}$ of units belonging to *other* linear chains is somewhat depleted in $V_r \sim r^d$: $\mathfrak{N} \simeq \phi_l V_r - g$. The relative depletion is therefore given by the factor $1 - \text{const}\,\frac{g}{\phi_l r^d}$. Nearly the same depletion factor applies to the concentration of ends, so

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[8] For $n \neq 1$ the exponential term $e^{-r/\xi}$ in brackets should be replaced by $(r/\xi)^{2-d}$, cf. eq. (134). This change, however, does not affect the argument presented here.

$$g_e(r) \sim 1 - \text{const}\,\frac{g}{\phi_l r^d} \sim 1 - \text{const}\,(r/\xi)^{2-d}\,, \quad r \gg \xi$$

which coincides with eq. (84).

The above treatment is valid as long as $N_m \gg N^*$, that is for

$$h \ll h^* \sim \tau^{(\nu d+\gamma)/2}$$

For $h \gg h^*$ (cf. Appendix B) we have $\xi_m \sim \xi$ and $N_m \sim N^*$ with $\xi \sim h^{-2\nu/(d\nu+\gamma)}$ (cf. eq. (B14)) and $N^* \sim \xi^{1/\nu_p} \sim h^{-2\phi_g/(\nu d+\gamma)}$. So

$$c_l(N) \sim h^2 N^{\gamma_p - 1} e^{-N/N_m}, \quad h \gtrsim h^* \tag{86}$$

(cf. eq. (74)). Using eqs. (75) we obtain

$$c_l \sim h^{2-2\gamma/(\nu d+\gamma)}, \;\; \phi_l \sim h^{2(\nu d-\phi_g)/(\nu d+\gamma)}, \quad h \gtrsim h^* \tag{87}$$

The above result for c_l is in agreement with $c_l \sim hm$ (cf. eq. (B4)) and with the hyperscaling relation $c_l\xi^d \sim 1$ corresponding to the picture[45] of marginally overlapping blobs (linear chain segments of size ξ). Further, eq. (87) for ϕ_l agrees with eqs. (B13), (18). These agreements provide an additional justification of the approach we take. The behavior of the total polymer concentration ϕ for large h can be obtained using eq. (62) and the scaling properties for the singular part of the magnetic free energy (see Appendix B):

$$\phi - \phi^* \sim h^{2(d\nu-1)/(d\nu+\gamma)}, \quad h \gtrsim h^* \tag{88}$$

The length distribution of rings for $h \ll 1$, $\tau \ll 1$ can be obtained on the similar grounds. The result for $h \ll h^*$ is (cf. eq. (67) valid for $\tau = h = 0$):

$$c_r(N) \sim \begin{cases} N^{-\nu_p d-1} & , \; N \lesssim N^* \\ (N^*)^{-\nu_p d-1}\,(N/N^*)^{-d/2-1}\, e^{-N/N_m} & , \; N \gtrsim N^* \end{cases} \tag{89}$$

where N_m is defined in eq. (77). For high $h \gg h^*$ we get

$$c_r(N) \sim N^{-\nu_p d-1} e^{-N/N_m} \tag{90}$$

with

$$N_m \sim h^{-2\phi_g/(d\nu+\gamma)}, \;\; h \gtrsim h^* \tag{91}$$

The properties of the system just before the polymerization transition, $\tau < 0$, can be established in exactly the same way. For $h \ll h^*$ the linear chains are rare. Their total concentration ϕ_l and number concentration c_l are (cf. eqs. (B12), (18), (B5)):

$$\phi_l \sim h^2\,|\tau|^{-\gamma-\phi_g}\,, \quad c_l \sim h^2\,|\tau|^{-\gamma}\,, \quad h < h^*$$

Thus, the mean (the terminal) length of linear chains is

$$N_m = \phi_l/c_l \sim |\tau|^{-\phi_g}\,, \;\; h \lesssim h^* \tag{92}$$

The chains do not overlap in this regime, hence their size $R(N) \sim N^{\nu_p}$ for $N \lesssim N_m$, and their length distribution is defined by the first line in eq. (74):

$$c_l(N) \sim h^2 N^{\gamma_p - 1} e^{-N/N_m}, \quad h \lesssim h^*$$

The same distribution is valid for $h > h^*$, however, with a different N_m defined in eq. (91). The concentrations c_l and ϕ_l for $h > h^*$ are still defined in eqs. (87). Note that the correlation length ξ is defined in eq. (B14), hence for $\tau < 0$ we always have $\xi \sim R(N_m) \sim N_m^{\nu_p}$, that is $\xi \sim \xi_m$ and $N^* \sim N_m$.

The length distribution of ring polymers for $\tau < 0$ is formally defined by eq. (90) with the same N_m as for linear chains (cf. eq. (92) for $h \lesssim h^*$, eq. (91) for $h \gtrsim h^*$).

We are now in a position to identify the whole τ-dependence of ϕ_l and $\phi_r = \phi - \phi_l$ for a given $h \ll 1$. Note that ϕ is defined in eq. (63) for $h \lesssim h^*$ and in eq. (88) for $h \gtrsim h^*$. Using the results obtained just above we find:

$$\phi_l \sim \begin{cases} h^2 \left|\tau\right|^{-\gamma - \phi_g} & , \ \tau < 0, \ \ |\tau| \gtrsim \tau^* \\ (\tau^*)^{\nu d - \phi_g} & , \qquad |\tau| \lesssim \tau^* \\ \tau^{\nu d - \phi_g} & , \qquad \tau \gtrsim \tau^* \end{cases} \tag{93}$$

where $\tau^* \sim h^{2/(\nu d + \gamma)}$, and

$$\phi_r - \phi^* \sim \begin{cases} -\left|\tau\right|^{\nu d - 1} - h^2 \left|\tau\right|^{-\gamma - \phi_g} & , \ \tau < 0, |\tau| \gtrsim \tau^* \\ -(\tau^*)^{\nu d - \phi_g} & , \qquad |\tau| \lesssim \tau^* \\ -\tau^{\nu d - \phi_g} & , \qquad \tau \gtrsim \tau^* \end{cases} \tag{94}$$

Note two competing terms in the first line of eq. (94): one term increases and the other decreases with $|\tau|$. The maximum of ϕ_r is thus achieved below the critical point ($\beta < \beta^*$) at $\tau = \tau_m < 0$, $|\tau_m| \sim (\tau^*)^{(\nu d + \gamma)/(\nu d + \gamma + \phi_g - 1)}$. The exponent $\phi_g > 1$ for $n > 0$, hence τ_m must be well outside the region $|\tau| \sim \tau^*$, where the properties of living polymers are defined mainly by the parameter h rather than τ.

Thus, the volume concentration of rings for $\tau < \tau_m$ is given by

$$\phi_r - \phi^* \sim - \left|\tau\right|^{\nu d - 1} \tag{95}$$

This is an interesting and counter-intuitive behavior: Recall that

$$\phi_r = \int N c_r(N) \mathrm{d}N$$

where

$$c_r(N) \simeq \mathrm{const}\, N^{-\nu_p d - 1} e^{-N/N_m} \tag{96}$$

and $N_m \sim |\tau|^{-\phi_g}$. As $|\tau|$ increases, say, by a factor of 2, the cut-off length N_m decreases by a similar factor, leading to a decrease of ϕ_r by $\Delta_t \phi_r \sim N_m^2 c_r(N_m) \sim |\tau|^{\nu d - \phi_g}$ due to the cut-off 'tail' of the ring length-distribution. As $\phi_g > 1$, the obtained $\Delta_t \phi_r$ is much larger than the actual change $\Delta \phi_r = \phi_r(\tau) - \phi_r(2\tau) \sim |\tau|^{\nu d - 1}$ defined in eq. (95). Therefore, what is lost at the tail, must be compensated somewhere in the middle. [9] This condition points to the universal distribution $c_r(N)$ of the following form

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[9] The compensation can not come just from the prefactor 'const' in eq. (96): this prefactor defines the concentration of small rings which must be an analytical function of both ϕ and τ, hence its change can not exceed $\sim |\tau|^{\nu d - 1}$, and thus it cannot balance $\Delta_t \phi_r$.

$$c_r(N) \sim N^{-\nu_p d-1} f_r(N/N_m)$$

where $f_r(x)$ must show a *maximum* at some $x \sim 1$ (i.e., $N \sim N_m$). [10]

5.2. The concentration correlation functions

The correlation function of concentration, $G_p(r)$, is defined in eq. (34). Let us analyze this function starting with the case $\tau \gg \tau^* \sim h^{2/(\nu d+\gamma)}$. By virtue of the fluctuation theorem, we have (see eq. (64))

$$\int G_p(r)\mathrm{d}^d r = \chi_p \equiv \partial\phi/\partial\tau \sim |\tau|^{d\nu-2} \tag{97}$$

As can be verified (based on eqs. (103), (104) below), the main contribution to the above integral comes from $r \sim \xi \sim \tau^{-\nu}$, hence

$$G_p(\xi) \sim \tau^{2\nu d-2} \tag{98}$$

Note that $G_p(\xi) \ll \phi_l^2 \sim \tau^{2\nu d-2\phi_g}$; this feature reflects the significant screening of concentration fluctuations associated with 'blobs' of linear chains (the screening is provided by the rings of size $\lesssim \xi$).

The function $G_p(r)$ can be also defined in magnetic terms (see eq. (35)): $G_p(r) \sim \langle\varphi(0)^2\varphi(r)^2\rangle - \langle\varphi^2\rangle^2$. As $\langle\varphi_1\rangle = m$, it is tempting to write $\varphi^2 - \langle\varphi^2\rangle \simeq 2m\delta\varphi_1$, where $\delta\varphi_1 = \varphi_1 - m$ and the terms $\sim \delta\varphi^2$ are neglected. This would lead to $G_p(r) \simeq 4m^2 G_1(r)$, and

$$G_p(\xi) \sim m^4 \tag{99}$$

since $G_1(\xi) \sim m^2$ (eq. (B15) shows that the fluctuations of the spin field $\varphi_1(r)$ at the length-scale $\sim \xi$ are comparable with the average magnetization). The same result, eq. (99), could be also obtained including the neglected terms ($\sim \delta\varphi^2$), but assuming Gaussian statistics of the field $\delta\varphi(r)$. It turns out, however, that eq. (99) is a dramatic overestimation: in fact eq. (98) says that $m^4 \sim \tau^{2(\nu d-\gamma)} \gg G_p(\xi) \sim \tau^{2(\nu d-1)}$ since $\tau \ll 1$ and $\gamma > 1$. This feature is due to strongly non-Gaussian character of fluctuations of $\varphi(r)$ at length scales $\lesssim \xi$.

For $n > 0$ the short-range concentration fluctuations are dominated by short rings whose volume fraction is finite at the critical point, so $G_p(1) \sim 1$. Taking this into account and assuming the scaling law, $G_p(r) \propto r^{-x}$ in the range $1 \ll r \ll \xi$, we find $x = 2/\nu - 2d$:

$$G_p(r) \sim r^{2/\nu-2d}, \quad 1 \ll r \lesssim \xi, \quad n > 0 \tag{100}$$

Note that the exponent here is significantly different from the analogous exponent for $G_1(r)^2$, eq. (B15). Eq. (100) remains valid in the whole fluctuation regime (and not only for $\tau \gg \tau^*$) with ξ defined in eq. (B14): [11]

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[10] It comes from the formal condition $\int_0^\infty x^{-\nu_p d-1} x^2 \mathrm{d}\left[f_r(x)\right] = 0$ on recalling that $f_r(0)$ is finite, while $f_r(x) \sim e^{-x}$ for $x \gg 1$.

[11] Note the general fluctuation relation: $\chi_p \sim \xi^{2/\nu-d}$, coming from eqs. (63), (88).

$$\xi \sim \begin{cases} |\tau|^{-\nu} & , \ |\tau| \gtrsim \tau^* \\ |\tau^*|^{-\nu} & , \ |\tau| \lesssim \tau^* \end{cases}$$

For $n = 0$ there are no rings, so $G_p(1) \sim \phi_l \sim \tau^{\nu d - 1}$ (as $\phi_g = 1$ for $n = 0$), so

$$G_p(r) \sim \phi r^{1/\nu - d}, \ \ 1 \ll r \lesssim \xi, \ \ n = 0$$

The behavior of $G_p(r)$ for longer r also crucially depends on n. If $n \neq 1$, $G_p(r)$ does not decay exponentially at $r \gtrsim \xi$, rather it shows a power-law decay, $G_p(r) \propto r^{-2d}$ for $r \gg \xi$, $h = 0$, $\tau > 0$ (cf. eq. (56)). For $h > 0$ this decay is cut-off at the terminal length-scale ξ_m corresponding to the size of the longest polymers with $\sim N_m$ units, $\xi_m \gg \xi$ for $\tau \gg \tau^*$ (cf. eq. (59):

$$G_p(r) \sim (n-1)\tau^{-2} r^{-2d} e^{-2r/\xi_m}, \ \ r \gg \xi, \ \ n \neq 1 \tag{101}$$

where $\xi_m \sim h^{-0.5} \tau^{(d\nu + \gamma)/4 - \nu}$ for $\tau \gg \tau^*$ and $\xi_m \sim \xi$ otherwise (cf. eq. (B16).

More precisely, using eq. (58) and noting that $\varkappa = \phi_l \partial\tau/\partial\phi_l \simeq \tau/(\nu d - \phi_g)$, we get the quantitative prediction of $G_p(r)$ for $d = 3$, $r \gg \xi$:

$$G_p(r) \simeq \frac{3(n-1)}{(4\pi)^2} (3\nu - \phi_g)^2 \tau^{-2} r^{-6} e^{-2r/\xi_m} \left\{ 1 + 2\frac{r}{\xi_m} + \frac{5}{3}\frac{r^2}{\xi_m^2} + \frac{2}{3}\frac{r^3}{\xi_m^3} + \frac{1}{6}\frac{r^4}{\xi_m^4} \right\} \tag{102}$$

The obtained short-range (eq. (100)) and long-range (eqs. (101), (102)) asymptotics of $G_p(r)$ smoothly cross over at $r \sim \xi$ giving $G_p(\xi)$ defined in eq. (98). Remarkably, $G_p(r)$ is non-monotonic for $n = 0$: it is positive for $r \ll \xi$ and negative for $r \gg \xi$, having a knot at $r \sim \xi$. It also shows the negative absolute minimum (anti-correlation shell) in the same region, $r \sim \xi$, as discussed in refs.[31,32]. By contrast, $G_p(r)$ is always positive and is monotonically decaying for $n > 1$.

For $n = 1$ the magnetic Hamiltonian $H_m[\varphi]$ does not generate any soft modes whose correlation length ξ_m diverges as $h \to 0$ (the transverse modes are absent). Hence, the system for $\tau > 0$ and $h > 0$ is still characterized by the only essential length scale ξ. For $r \gg \xi$ the fluctuations are small, so the correlation functions $G_1(r)$, $G_e(r)$, $G_p(r)$ (see eqs. (25), (41), (35)) follow essentially the mean-field laws, albeit with the fluctuation-renormalized parameters (cf. eq. (B15)):

$$G_e(r) \propto G_1(r) \propto G_p(r) \propto r^{2-d} e^{-r/\xi}, \ \ r \gg \xi, \ \ n = 1$$

The revealed behavior of the concentration correlation function can be summarized as follows:

$$G_p(r) \simeq \xi^{2/\nu - 2d} g_p(r/\xi, n, d) \ \text{ for } \ \tau \gg \tau^* \ \text{ and } \ r \ll \xi_m \tag{103}$$

where $g_p(x, n, d)$ is a universal function,

$$g_p(x, n, d) \sim x^{2/\nu - 2d}, \quad x \ll 1$$

and

$$g_p(x, n, d) \sim \begin{cases} (n-1)x^{-2d} & , \ n \neq 1, \ \ x \gg 1 \\ x^{2-d} e^{-x} & , \ n = 1, \ \ x \gg 1 \end{cases} \tag{104}$$

The long-range power-law regime, $G_p \propto r^{-2d}$, becomes irrelevant for $\tau \lesssim \tau^*$ and for $\tau < 0$ since the two length-scales ξ and ξ_m are nearly the same in this region.

Thus, the function $G_p(r)$ for $n \neq 1$ and $\tau \gg \tau^*$ is characterized by two correlation lengths, ξ and $\xi_m \gg \xi$. This feature reflects the coupling of φ^2 (cf. eq. (35)) with both longitudinal (φ_1) modes and with much softer transverse (φ_2) modes, associated with length-scales, ξ and ξ_m, respectively.

5.3. Correlation function of linear chain concentration

We denote this function $G_{pl}(r) = \langle\phi_l(0)\phi_l(r)\rangle - \phi_l^2$, where $\phi_l(r)$ is the local concentration of units belonging to linear chains. Obviously $G_{pl}(r) = G_p(r)$ for $n = 0$ as there are no rings in this case. Let us turn to living systems with rings, $n > 0$. Surprisingly, as we show below, the two functions, G_{pl} and G_p, are dramatically different in the latter case. As before, we focus on the regime $\tau \gg \tau^*$ (i.e., $h \ll h^*$).

To calculate $G_{pl}(r)$ let consider the real-space polymer system and label all units of linear chains by black colour, all other units (belonging to rings) being labelled as 'white'. The correlation function $G_{pl}(r) = \phi_l\delta(\underline{r}) + \phi_l g_{pl}(r) - \phi_l^2$, where $g_{pl}(r)$ is the conditional probability to have a black unit at $\underline{r}$ provided that another black unit is located at the origin. For $r \ll \xi$ the concentration of black units at $\underline{r}$, $c_b(r)$, is dominated by the units of the very same chain that pass through the origin (in fact, in this regime $c_b(r)$ is much higher than ϕ_l, while the contribution of units belonging to other chains is much smaller than ϕ_l, cf. eq. (85)). Therefore $g_{pl}(r) \sim r^{1/\nu_p - d}$ for $r \ll \xi$, where r^{1/ν_p} is about the number of units in a chain segment (blob) of size r, so

$$G_{pl}(r) \sim \phi_l r^{\phi_g/\nu - d} \sim \phi_l^2 \left(r/\xi\right)^{\phi_g/\nu - d}, \quad 1 \lesssim r \lesssim \xi$$

where $\phi_l \sim \tau^{\nu d - \phi_g}$. Note that the exponent $\phi_g/\nu - d$ characterizing the scaling dependence of $G_{pl}(r)$ is significantly different from the analogous exponent, $2/\nu - 2d$, for the function $G_p(r)$ for $n > 0$.

Let us turn to longer length-scales, $r \gg \xi$, where the fluctuations always follow essentially the mean-field laws (see sections 3, 4). The function $G_{pl}(r)$ in this regime is calculated in Appendix E. It is shown there that the long-range part of $G_{pl}(r)$ is defined by the fluctuations of the volume fraction of large rings (i.e., by the structure factor of rings). Using the general result, eq. (E3), we find for $d = 3$

$$G_{pl}(r) \simeq \frac{n}{32\pi^2} a^{*-4} r^{-2} e^{-2r/\xi_m}, \quad r \gg \xi, \ \ n > 0$$

and for any d

$$G_{pl}(r) \sim n a^{*-4} r^{4-2d}, \quad \xi_m \gg r \gg \xi, \ \ n > 0 \tag{105}$$

Interestingly, for $n \neq 0, 1$ the function $G_{pl}(r)/\phi_l$ is rather similar to $G_1(r)$ (cf. eq. (C10)). Note that $G_{pl}(r)$ is roughly the square of the typical amplitude, $\delta\phi_l^r$, of fluctuations of the field ϕ_l smoothed over the length-scale r, hence

$$\delta\phi_l^r \sim a^{*-2} r^{2-d}, \quad \xi \lesssim r \lesssim \xi_m$$

This result for $\delta\phi_l^r$ can be interpreted within the blob picture as the mean concentration provided by a chain segment (blob) of size $\sim r$.

Note also that $G_{pl}(r) \gg G_p(r)$ for $r \gtrsim \xi$, $n > 0$ (cf. eqs. (105), (101)) since $\xi^2/a^{*2} \sim N^* \sim \tau^{-\phi_g} \gg \tau^{-1}$ (as $\phi_g > 1$ for $n > 0$). Thus, the long range fluctuations of concentration of 'black' units (belonging to linear chains) are much stronger than fluctuations of the total concentration. To conclude, the function $G_{pl}(r)$ for living polymers with rings ($n > 0$) is qualitatively different from the correlation function of the total concentration, $G_p(r)$, at all length-scales ($r \ll \xi$ and $r \gg \xi$).

Using eq. (E3) we get the structure factor of linear chains at $q = 0$: $S_{pl}(0) = \int G_{pl}(r)\mathrm{d}^d r \simeq \frac{n}{2}(4\pi)^{-d/2} a^{*-d} N_m^{2-d/2}$. Thus, $S_{pl}(0) \propto h^{d/2-2}$ diverges at $h \to 0$ at any $\tau > 0$ in contrast to $\partial\phi_l/\partial\tau$ which remains finite in this regime ($h \to 0$, $\tau > 0$). [12]

6. Further generalizations and summary of the main results.

1. The Ginzburg parameter. In the preceding sections we analyzed the thermodynamic properties and correlation functions characterizing solutions of living polymers in two major regimes: mean-field regime (see sections 3, 4) and fluctuation regime (see section 5). The systems are characterized by the two main parameters: $\tau = \ln(\beta/\beta^*) = \mu - \mu^*$, the deviation of the monomer unit chemical potential, $\mu = \ln\beta$, from the critical value μ^*, and $h = e^{-E}$, where E is the excess free energy of a chain end (end-cap energy), and $2E$ is the chain scission energy (note that all energy quantities are expressed in $k_B T$ units). The fluctuation regime occurs close to the critical point ($\beta = \beta^*$, $h = 0$), $|\tau| \lesssim \tau_c \sim 1/z^{*2}$ (for $d = 3$), while the mean-field domain emerges farther from this point, $|\tau| \gg \tau_c$ (cf. eq. (11)). The latter condition is equivalent to the Ginzburg criterion of validity of the mean-field description[49] for the relevant magnetic model, eq. (B1), in d-dimensional space:

$$\mathrm{Gi} = |\tau|^{d-4} (z^*)^{-2} \ll 1 \tag{106}$$

where Gi is the Ginzburg parameter[50], $z^* \sim b^d$ and the length b is defined in eq. (24). Thus, in the general case

$$\tau_c \sim (z^*)^{-2/(4-d)} \tag{107}$$

Normally, the effective number z^* of neighbors of a given site is large, hence $\tau_c \ll 1$ (note that $z^* \sim b^3/v$ for $d = 3$, where v is excluded volume for monomer unit).

2. The basic length-scales and concentrations in the mean-field regime. Let us now summarize the main results obtained in the mean-field regime, $\tau_c \ll |\tau| \ll 1$, for the volume concentration of linear chains ϕ_l, the mean polymerization index of linear chains N_m, the correlation lengths ξ and ξ_m, the concentration of chain ends $c_e = 2c_l$, and the polymerization index (molecular mass) distributions of rings and linear chains, $c_r(N)$, $c_l(N)$ for $N \gg 1$ (cf. eqs. (9), (32), (14), (27), (31), (15)). Above the polymerization transition, $\tau > 0$, the effect of h on ϕ_l is weak for $h \ll h^*(\tau) \sim \tau^{3/2}$. In this regime

$$\phi_l \simeq 1 - e^{-\tau} \simeq \tau, \quad c_e = 2c_l \simeq h\sqrt{2\tau} \tag{108}$$

$$N_m \simeq \sqrt{2\phi_l}/h \simeq \sqrt{2\tau}/h \tag{109}$$

$$\xi^2 \simeq a^2/(2\tau), \quad \xi_m^2 \simeq a^2 N_m \simeq \sqrt{2\tau}\, a^2/h \tag{110}$$

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[12] And, of course, $S_{pl}(0)$ and $\partial\phi_l/\partial\tau$ do not coincide.

Note that the condition $h \ll h^*(\tau)$ is equivalent to $\xi \ll \xi_m$ saying that typical linear chains are long enough. Thus, the crossover field h^* corresponds to $\xi \sim \xi_m$.

Eqs. (108), (109), (110) are valid for $\tau \gg \tau^*(h) \sim h^{2/3}$. For $|\tau| \lesssim \tau^*$ (that is for $1 \gg h \gtrsim h^* \sim |\tau|^{3/2}$) the properties of the system are dominated by the parameter h (end-cap energy), being almost independent of τ:

$$\phi_l \sim \tau^* \sim h^{2/3}, \;\; c_l \sim h^{4/3}, \;\; N_m \sim h^{-2/3}, \;\; \xi \sim \xi_m \sim a h^{-1/3}, \;\; |\tau| \lesssim \tau^* \tag{111}$$

The results of section 3.4 allow to find N_m, ξ, ξ_m also for $\tau < 0$, $|\tau| \gg \tau^*$:

$$N_m \simeq 1/|\tau|, \;\; \xi^2 \simeq \xi_m^2 \simeq a^2/|\tau|, \;\; h^{2/3} \ll |\tau| \ll 1 \tag{112}$$

The length distributions for linear chains and rings, valid for $|\tau| \ll 1$, are

$$c_l(N) \simeq \frac{1}{2} h^2 e^{-N/N_m} \tag{113}$$

$$c_r(N) \simeq \frac{n}{2}\frac{1}{N}\left(4\pi N a^2\right)^{-d/2} e^{-N/N_m}, \;\; N \gg 1 \tag{114}$$

The concentrations c_l, ϕ_l are defined by $c_l(N)$:

$$c_e = 2c_l \simeq h^2/|\tau|, \;\; \phi_l \simeq 0.5 h^2/\tau^2, \;\; \tau < 0, \;\; |\tau| \gg \tau^*$$

while for $\tau > 0$ we recover eqs. (108).

The total volume concentration of rings for $\tau_c \ll |\tau| \ll 1$ can be then found either using the distribution $c_r(N)$ or using eq. (32):

$$\phi_r \simeq \phi^* - \frac{\Gamma(2-d/2)}{d/2-1}\frac{n}{2}\left(4\pi a^2\right)^{-d/2} N_m^{1-d/2} \tag{115}$$

where ϕ^* is the total concentration at the transition point ($\tau = 0$, $h = 0$, $N_m \to \infty$), $\phi^* \sim n/z^*$. Using eq. (115) we get:

$$\phi^* - \phi_r \sim (n/z^*)\,|\tau|^{d/2-1}, \;\; \tau < 0, |\tau| \gtrsim \tau^* \tag{116}$$

$$\phi^* - \phi_r \sim (n/z^*)\left(h/\sqrt{\tau}\right)^{d/2-1}, \;\; \tau \gtrsim \tau^* \tag{117}$$

Taking into account the fluctuation correction $\sim (1/z^*)^2$ for ϕ_r we get

$$\phi^* - \phi_r \sim \left(n/z^{*2}\right)\tau^{d-3} + (n/z^*)\left(h/\sqrt{\tau}\right)^{d/2-1} - n\tau_c, \;\; \tau \gtrsim \tau^* \tag{118}$$

The last term here represents the fluctuation correction for ϕ^*. [13] For smaller τ we have (cf. eq. (116))

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[13] Note that the critical concentration ϕ^*, being located in the fluctuation zone, cannot be predicted precisely in terms of the mean-field expansion as a series of $1/z^*$. The fluctuation correction to ϕ^* is $\sim \tau_c \sim (z^*)^{-2/(4-d)}$; it is negative reflecting ring swelling due to some repulsion of its segments.

$$\phi^* - \phi_r \sim \begin{cases} (n/z^*)\,(\tau^*)^{d/2-1} & , \quad |\tau| \lesssim \tau^* \\ (n/z^*)\,|\tau|^{d/2-1} & , \ \tau < 0, |\tau| \gtrsim \tau^* \end{cases} \tag{119}$$

where $\tau^* \sim h^{2/3}$. Note that $\phi^* - \phi_r$ for $\tau < 0$ is comparable with the concentration contribution of large rings (of size $\gtrsim \xi$). The mean-field dependence of ϕ_l on τ, h can be summarized as

$$\phi_l \sim \begin{cases} \tau & , \quad \tau \gtrsim \tau^* \\ \tau^* & , \quad |\tau| \sim \tau^* \\ h^2/\tau^2 & , \ \tau < 0, |\tau| \gtrsim \tau^* \end{cases} \tag{120}$$

Therefore, the excess total concentration $\phi - \phi^* = \phi_l + \phi_r - \phi^*$ is

$$\phi - \phi^* \sim \begin{cases} \tau & , \quad \tau \gtrsim \tau^* \\ \tau^* & , \quad |\tau| \sim \tau^* \\ h^2/\tau^2 - (n/z^*)\,|\tau|^{d/2-1} & , \ \tau < 0, |\tau| \gtrsim \tau^* \end{cases} \tag{121}$$

The results summarized above suggest that in the general case ($h \neq 0$, $\tau \neq 0$) the mean-field theory is valid if either $|\tau|$ or τ^* exceed τ_c:

$$|\tau| + \tau^* \gg \tau_c$$

The latter condition is equivalent to stating that the correlation length ξ is short enough:

$$\xi \ll r_c, \quad r_c \sim a\,(z^*)^{1/(4-d)} \tag{122}$$

where r_c is the characteristic mean-field length-scale. It is important that the mean-field approach is ***always*** applicable at short length scales, $r \ll r_c$, even at the critical point. In fact, based on the magnetic Hamiltonian, eq. (B1) or eq. (B2), it is easy to show that the short-length modes of fluctuations of the field $\varphi(r)$ (with wave-length $\ll r_c$) are always nearly Gaussian: the quadratic part of the Hamiltonian is sufficient to describe this regime.

3. The concentrations ϕ, ϕ_l, ϕ_r in the critical regime.

Considering the critical regime ($|\tau| + \tau^* \lesssim \tau_c$) so far we did not pay attention to z^* focusing mainly on the τ- and h-scaling dependencies. Below we account for the effect of z^* in the fluctuation regime. To this end, in most cases it is sufficient to demand a smooth crossover between the mean-field and fluctuation regimes at $\tau \sim \tau_c$, or at $r \sim r_c$. First, we note that the mean-field result, $\tau^*(h) \sim h^{2/3}$ is valid for $h \gtrsim h_c$, where

$$h_c \sim \tau_c^{3/2} \sim (z^*)^{-3/(4-d)} \tag{123}$$

is the threshold beyond which the correlation length ξ is shorter than r_c (so, the mean-field theory is always applicable for $h \gg h_c$). Thus, applying the scaling result for τ^* in the fluctuation regime (see the line below eq. (93)), we get generally $\tau^*(h) \sim h^{2/3}$ for $h \gtrsim h_c$ and

$$\tau^*(h) \sim \tau_c\,(h/h_c)^{2/(\nu d + \gamma)}, \quad h \lesssim h_c \tag{124}$$

In what follows we consider the regime $h \lesssim h_c$, hence $\tau^* = \tau^*(h) \lesssim \tau_c$. Matching the mean-field and fluctuation results for ϕ_l, eqs. (120) and (93), yields

$$\phi_l \sim \begin{cases} \tau & , \quad \tau \gtrsim \tau_c \\ \tau_c \left(\tau/\tau_c\right)^{\nu d-\phi_g} & , \quad \tau^* \lesssim \tau \lesssim \tau_c \\ \tau_c \left(\tau^*/\tau_c\right)^{\nu d-\phi_g} & , \quad |\tau| \lesssim \tau^* \\ h^2 \tau_c^{\gamma+\phi_g-2} \left|\tau\right|^{-\gamma-\phi_g} & , \quad \tau < 0, \tau^* \lesssim |\tau| \lesssim \tau_c \\ h^2/\tau^2 & , \quad \tau < 0, |\tau| \gtrsim \tau_c \end{cases} \tag{125}$$

Similarly, we get for ϕ using eqs. (121), (63), (88):

$$\phi - \phi^* \sim \begin{cases} \tau & , \quad \tau \gtrsim \tau_c \\ \tau_c \left(\tau/\tau_c\right)^{\nu d-1} & , \quad \tau^* \lesssim \tau \lesssim \tau_c \\ \tau_c \left(\tau^*/\tau_c\right)^{\nu d-1} & , \quad |\tau| \lesssim \tau^* \\ -\tau_c \left(|\tau|/\tau_c\right)^{\nu d-1} & , \quad \tau < 0, \tau^* \lesssim |\tau| \lesssim \tau_c \\ -(n/z^*) \left|\tau\right|^{d/2-1} & , \quad \tau < 0, |\tau| \gtrsim \tau_c \end{cases} \tag{126}$$

The total concentration ϕ thus monotonically increases with τ, showing a complicated behavior involving power laws with the exponents $d/2-1$, $\nu d-1$, 1. Based on the above equations we also get the polymer osmotic compressibility $\chi_p \equiv \partial\phi/\partial\tau$:

$$\chi_p \sim \begin{cases} 1 & , \quad \tau \gtrsim \tau_c, \\ \left(|\tau|/\tau_c\right)^{\nu d-2} & , \quad \tau^* \lesssim |\tau| \lesssim \tau_c \\ \left(\tau^*/\tau_c\right)^{\nu d-2} & , \quad |\tau| \lesssim \tau^* \end{cases} \tag{127}$$

Eqs. (127) are valid as long as $\alpha = 2 - \nu d > 0$. For $d = 3$ this is true for $n = 0$ and $n = 1$. In these cases χ_p diverges at the critical point (for $h = 0$). By contrast, the exponent $\alpha < 0$ for $n \geq 2$, so the compressibility χ_p does not diverge at $\tau \to 0$ (for $h = 0$): it remains finite for any τ (Fig. 5). As a result, eqs. (127) must be replaced by just $\chi_p \sim 1$ for $n \geq 2$ (neglecting singular but small critical corrections), so in this case we have $\phi - \phi^* \sim \tau$ in the whole region $|\tau| \ll 1$ instead of eqs. (126). Thus, a small increase of the chemical potential $\mu = \ln\beta$ above μ^* in the fluctuation regime ($\tau < \tau_c$, $d = 3$) leads to an increase of the total concentration by

$$\Delta\phi = \phi - \phi^* \propto \tau^{1-\alpha} \approx \tau^{0.89} \text{ for } n = 1, \; \Delta\phi \propto \tau \text{ for } n = 2 \tag{128}$$

The corresponding concentrations of linear chains are always higher for small τ (cf. the second line in eq. (125)):

$$\phi_l \propto \tau^{0.80} \text{ for } n = 1, \; \phi_l \propto \tau^{0.83} \text{ for } n = 2 \tag{129}$$

Turning to the fraction of rings, we find using eqs. (118), (119), (94)

$$\phi^* - \phi_r \sim n\tau_c \cdot \begin{cases} \left(\tau/\tau_c\right)^{d-3} + \left(h/h_c\right)^{\frac{d-2}{2}} \left(\tau/\tau_c\right)^{\frac{2-d}{4}} - 1 & , \quad \tau \gtrsim \tau_c \\ \left(\tau/\tau_c\right)^{\nu d-\phi_g} & , \quad \tau^* \lesssim \tau \lesssim \tau_c \\ \left(\tau^*/\tau_c\right)^{\nu d-\phi_g} & , \quad |\tau| \lesssim \tau^* \\ h^2 \tau_c^{-3} \left(\tau_c/|\tau|\right)^{\gamma+\phi_g} + \left(|\tau|/\tau_c\right)^{\nu d-1} & , \quad \tau < 0, \tau^* \lesssim |\tau| \lesssim \tau_c \\ \left(|\tau|/\tau_c\right)^{d/2-1} & , \quad \tau < 0, |\tau| \gtrsim \tau_c \end{cases} \tag{130}$$

Thus, $\phi^* - \phi_r$ has a minimum (corresponding to local maximum of the ring volume concentration ϕ_r) in the region $\tau < 0$, $\tau^* \lesssim |\tau| \lesssim \tau_c$, more precisely, at $\tau = \tau_m$,

$|\tau_m| \sim \tau_c \left(h/h_c\right)^{2/(\nu d+\gamma+\phi_g-1)}$. For $d \leq 3$ the concentration ϕ_r also shows a local minimum at $\tau \sim \tau_c$. The overall dependence of ϕ_r on the chemical potential $\mu = \tau + \ln\beta^*$ is therefore non-monotonic: ϕ_r decreases with μ near the critical point (at small $|\tau|$) and it increases with μ outside the critical region (both below and above the critical point).

Note that eq. (125) is valid for any n, while the above equations for $\phi - \phi^*$ and $\phi_r - \phi^*$ are valid only for $n > 0$. In the special case $n = 0$ we have $\phi^* = 0$, $\phi_r = 0$, and $\phi = \phi_l$ (with the exponent $\phi_g = 1$).

4. The general summary on the main length-scales and mass distributions for linear chains and rings.

The behavior of the correlation lengths ξ, ξ_m in the critical region $\tau \lesssim \tau_c$, $h \lesssim h_c$ can be found in a similar way. Matching eqs. (110), (112), (111) with eqs. (B14), (B16) we get

$$\xi \sim \begin{cases} a/\sqrt{\tau} & , \quad |\tau| \gtrsim \tau_c \\ r_c\left(\tau/\tau_c\right)^{-\nu} & , \quad \tau^* \lesssim |\tau| \lesssim \tau_c \\ r_c\left(h/h_c\right)^{-2\nu/(\nu d+\gamma)} & , \quad |\tau| \lesssim \tau^* \end{cases}$$

$$\xi_m^2 \sim \begin{cases} \sqrt{2\tau}\, a^2/h & , \quad \tau \gtrsim \tau_c \\ r_c^2\left(h_c/h\right)\left(\tau/\tau_c\right)^{(\nu d+\gamma)/2-2\nu} & , \quad \tau^* \lesssim \tau \lesssim \tau_c \\ \xi^2 & , \quad \text{otherwise} \end{cases} \tag{131}$$

where τ_c, h_c, r_c and $\tau^* = \tau^*(h)$ are defined in eqs. (107), (123), (122), (124), respectively.

Let us turn to the size $R(N)$ of an N-chain (linear or cyclic). The chain statistics is always nearly Gaussian for $|\tau| \gg \tau_c$. Hence [14]

$$R(N) \sim a\sqrt{N}, \quad |\tau| \gg \tau_c$$

In the fluctuation regime, $|\tau| \lesssim \tau_c$, there are 3 characteristic polymerization numbers, N_c, N^* and N_m, associated with the lengths r_c, ξ and ξ_m, such that $R(N_c) \sim r_c$, $R(N^*) \sim \xi$ and $R(N_m) \sim \xi_m$. The chain statistics is Gaussian for $N \ll N_c$ and for $N \gg N^*$ (with renormalized parameters in the latter regime), hence

$$R(N) \sim \begin{cases} a\sqrt{N} & , \quad N \lesssim N_c \\ r_c\left(N/N_c\right)^{\nu_p} \sim \xi\left(N/N^*\right)^{\nu_p} & , \quad N_c \lesssim N \lesssim N^* \\ \xi\sqrt{N/N^*} \sim a^*\sqrt{N} & , \quad N \gtrsim N^* \end{cases}$$

where $\nu_p = \nu/\phi_g$,

$$N_c \sim 1/\tau_c \sim \left(z^*\right)^{2/(4-d)}$$

$$N^* \sim \begin{cases} 1/\tau & , \quad |\tau| \gtrsim \tau_c \\ N_c\left(\tau/\tau_c\right)^{-\phi_g} & , \quad \tau_c \gtrsim |\tau| \gtrsim \tau^* \\ N_c\left(h/h_c\right)^{-2\phi_g/(\nu d+\gamma)} & , \quad |\tau| \lesssim \tau^* \end{cases}$$

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[14] We do not consider untypically long chains with N much greater than N_m: their concentration is always extremely small.

and the renormalized statistical segment, $b^* = \sqrt{2d}a^*$, is

$$b^* \sim \begin{cases} b & , \quad |\tau| \gtrsim \tau_c \\ b\,|\tau/\tau_c|^{-\nu+\phi_g/2} & , \quad \tau_c \gtrsim |\tau| \gtrsim \tau^* \\ b\,|\tau^*/\tau_c|^{-\nu+\phi_g/2} & , \quad |\tau| \lesssim \tau^* \end{cases} \tag{132}$$

Note that N^* defines the size of the concentration blob for linear chains in the fluctuation regime: $\phi_l \sim N^*/\xi^d$ for $0 < \tau \lesssim \tau_c$.

The terminal length of linear chains, $N_m \sim \xi_m^2/a^{*2}$, since $R(N)^2 \sim a^{*2}N$ for $N \gtrsim N^*$:

$$N_m \sim \begin{cases} \sqrt{\tau}/h & , \quad \tau \gtrsim \tau_c \\ (h_c/h)\, N^* \,(\tau/\tau_c)^{(\nu d+\gamma)/2} & , \quad \tau_c \gtrsim \tau \gtrsim \tau^* \\ N^* & , \quad \text{otherwise} \end{cases}$$

The molecular mass (polymerization index) distributions for linear and cyclic chains, $c_l(N)$ and $c_r(N)$, can be also found based on the results considered above. In the mean-field regime, $|\tau| \gtrsim \tau_c$, the distributions are defined in eqs. (113), (114), while in the fluctuation regime we have (cf. eqs. (68), (74), (86))

$$c_l(N) \sim \begin{cases} h^2 e^{-N/N_m} & , \quad N \lesssim N_c \\ h^2\,(N/N_c)^{\gamma_p-1}\, e^{-N/N_m} & , \quad N_c \lesssim N \lesssim N^* \\ h^2\,(N^*/N_c)^{\gamma_p-1}\, e^{-N/N_m} & , \quad N^* \lesssim N \end{cases}$$

where $\gamma_p = \gamma/\phi_g$ is the polymer exponent, and (cf. eqs. (89), (90))

$$c_r(N) \sim nN^{-1}R(N)^{-d}e^{-N/N_m} \tag{133}$$

The total volume concentrations ϕ_l, ϕ_r, ϕ (cf. eqs. (125), (126), (130)) are consistent with these distributions (that is, $\phi_l \simeq \int N c_l(N)\mathrm{d}N$, etc.).

5. Correlation functions in the mean-field regime. Let us now discuss the correlation functions. We considered 2 magnetic functions $G_1(r)$ and $G_2(r)$ (for longitudinal and transverse modes of the field φ) and 4 polymer functions $G_e(r)$, $F_e(r)$, $G_p(r)$, $G_{pl}(r)$ (for concentrations of all chain ends, ends of the same chain, all monomer units, and units of linear chains). In the mean-field regime, $\tau \gg \tau_c$, the predictions for $d = 3$ are (cf. eqs. (26), (C3), (30):

$$G_1(r) \simeq \frac{1}{4\pi a^2 r}e^{-r/\xi} + \frac{n-1}{4\phi_l}\left(\frac{1}{4\pi a^2 r}\right)^2 e^{-2r/\xi_m}H(r-\xi), \quad r \gg b \tag{134}$$

where the factor $H(r-\xi)$ ($=1$ for $r > \xi$, $=0$ otherwise) serves to formally remove the second term for $r < \xi$. The function $G_1(r)$ is thus characterized by the standard Ornstein-Zernike correlation length ξ (the first term) and (for $n \neq 1$) the second long-range term with the length $\xi_m \gg \xi$. The transverse function is

$$G_2(r) \simeq \frac{1}{4\pi a^2 r}e^{-r/\xi_m}, \quad r \gg b \tag{135}$$

Thus, $G_1(r) \simeq G_2(r) \simeq \frac{1}{4\pi a^2 r}$ for $b \ll r \ll \xi$ (note that $\frac{1}{4\pi a^2 r}$ should be replaced with $\sim b^{-2}r^{2-d}$ in d-dimensions). For $0 < r \lesssim b$ the prediction is $G_{1,2}(r) \sim \frac{1}{z^*}$.

The polymer end-correlation functions, $G_e(r)$ and $F_e(r)$, are related to the magnetic functions for $r > 0$: $G_e(r) \simeq h^2 G_1(r)$ and $F_e(r) \simeq h^2 G_2(r)$ (cf. eqs. (42)), thereby they show the similar short range and long-range behaviors ($G_e(r) \simeq F_e(r)$ for $r \ll \xi$). This means that the short-range pair correlations of chain ends are dominated by the intra-chain contribution (due to pairs of ends of the same chain). For $r = 0$ the function G_e is significantly higher than for $r = 1$: $G_e(0) \simeq c_e \simeq hm \simeq h\sqrt{2\phi_l}$, while $G_e(1) \sim h^2/z^*$, so $G_e(1)/G_e(0) \sim h/\left(z^*\sqrt{\phi_l}\right) \ll 1$ for $h \ll 1$, $\phi_l \gg \tau_c$, $d = 3$.

The mean-field polymer concentration correlation functions for $d = 3$ and $\tau_c < \tau \ll 1$ are (cf. eqs. (60), (58)):

$$G_p(r) \simeq \left(\frac{\phi_l}{2\pi a^2 r} + \frac{n}{32\pi^2 a^4 r^2}\right) e^{-r/\xi} +$$

$$+H(r-\xi)3(n-1)(4\pi\phi_l)^{-2} r^{-6} e^{-2r/\xi_m} P(r/\xi_m), \tag{136}$$

where $P(r/\xi_m) = 1 + 2\frac{r}{\xi_m} + \frac{5}{3}\frac{r^2}{\xi_m^2} + \frac{2}{3}\frac{r^3}{\xi_m^3} + \frac{1}{6}\frac{r^4}{\xi_m^4}$. The correlation function for linear chains reads

$$G_{pl}(r) \simeq \frac{\phi_l}{2\pi a^2 r} e^{-r/\xi} + H(r-\xi)\frac{n}{32\pi^2 a^4 r^2} e^{-2r/\xi_m}, \tag{137}$$

The above equations are valid for $r \gg a$ and $n > 0$. The first term in $G_p(r)$, which is $\propto r^{-1}$, reflects the short-range contribution of linear chains, the next term, $\propto r^{-2}$, represents the effect of small rings, while the last long-range term, $\propto r^{-6}$, is generally due to both linear chains and large rings. The contribution of rings dominates at short scales, for $r \ll \tilde{r} \sim 1/(\phi_l a^2)$, where $\tilde{r}$ is the concentration blob size for linear chains. Similarly, the first term in eq. (137) corresponds to self-screened fluctuations of Gaussian segments of linear chains, while the second term is primarily due to fluctuations of large rings at nearly constant total concentration ϕ. For $n = 0$ the two functions are equal:

$$G_p(r) = G_{pl}(r) \simeq \frac{\phi}{2\pi a^2 r} e^{-r/\xi} - H(r-\xi)\frac{3}{(4\pi\phi_l)^2}\frac{1}{r^6} e^{-2r/\xi_m} P(r/\xi_m)$$

The functions $G_p(r)$ for $n = 0$, 1, 2 are shown in Fig. 6.

6. Correlation functions in the fluctuation regime. Let turn to the fluctuation regime above the polymerization transition, $0 < \tau \ll \tau_c$, $h \ll h_c$. The correlation functions can be obtained here, as before, matching the mean-field and scaling results at $r \sim r_c$. Thus, we get:

$$G_e(r) \sim \begin{cases} \frac{h^2}{4\pi a^2 r^{d-2}} e^{-r/\xi} & , \quad r \lesssim r_c \\ \frac{h^2}{a^2 r_c^{d-2}} \left(r/r_c\right)^{\gamma/\nu - d} e^{-r/\xi} & , \quad r_c \lesssim r \lesssim \xi \\ \frac{1}{2}\frac{n-1}{\xi_m^4}\left(\frac{1}{4\pi r}\right)^{2d-4} e^{-2r/\xi_m} & , \quad r \gg \xi \end{cases} \tag{138}$$

The above equation is valid for $n \neq 1$. Otherwise (for $n = 1$) the last line there should be replaced by

$$G_e(r) \simeq \frac{2\phi_l}{4\pi N_m \xi_m^2 r^{d-2}} e^{-r/\xi}, \quad r \gg \xi$$

Similarly

$$F_e(r) \sim \begin{cases} \frac{h^2}{4\pi a^2 r^{d-2}} e^{-r/\xi_m} & , \quad r \lesssim r_c \\ \frac{h^2}{a^2 r_c^{d-2}} \left(r/r_c\right)^{\gamma/\nu-d} e^{-r/\xi_m} & , \; r_c \lesssim r \lesssim \xi \\ \frac{2\phi_l}{4\pi N_m \xi_m^2 r^{d-2}} e^{-r/\xi_m} & , \quad r \gg \xi \end{cases} \tag{139}$$

Turning to the correlation function $G_p(r)$ for $n > 0$, we note that the mean-field length $\tilde{r}$ increases as τ is decreased, and tends to $\tilde{r} \sim \xi$ at $\tau \sim \tau_c$. Therefore, in the fluctuation regime, $\tau \ll \tau_c$, the short-range concentration correlations (for $r \lesssim \xi$) are always dominated by short rings that are Gaussian for $r \ll r_c$, and are swollen for $r_c \lesssim r \lesssim \xi$. Thus, for $n \neq 0, 1$ we obtain:

$$G_p(r) \sim \begin{cases} (n/32\pi^2)\, a^{-4} r^{4-2d} & , \quad r \lesssim r_c \\ a^{-4} r_c^{4-2d} (r/r_c)^{2/\nu-2d} & , \; r_c \lesssim r \lesssim \xi \\ 3(4\pi)^{-2}(n-1)(\tau+\tau^*)^{-2} r^{-2d} e^{-2r/\xi_m} & , \quad r \gtrsim \xi \end{cases} \tag{140}$$

In the last line here we took into account that $\varkappa = \phi_l \partial\tau/\partial\phi_l \sim \tau + \tau^*$ for $0 < \tau \ll 1$ (cf. eq. (125)). For $n = 1$ the last line in the above equation must be replaced by the standard long-range decay

$$G_p(r) \sim a^{-4} r_c^{4-2d} \left(\tau/\tau_c\right)^{2\nu d-2} \left(\xi/r\right)^{d-2} e^{-r/\xi}, \quad r \gtrsim \xi$$

Note that the susceptibility relation, eq. (97), is satisfied since $\xi^d G_p(\xi) \sim \chi_p$ (cf. eq. (127)).

The correlation function of linear chain concentration is

$$G_{pl}(r) \sim \begin{cases} (1/2\pi)\phi_l a^{-2} r^{2-d} e^{-r/\xi} & , \quad r \lesssim r_c \\ \phi_l^2 \left(r/\xi\right)^{\phi_g/\nu-d} & , \; r_c \lesssim r \lesssim \xi \\ (n/32\pi^2)\, a^{*-4} r^{4-2d} e^{-2r/\xi_m} & , \quad r \gtrsim \xi \end{cases} \tag{141}$$

For $n = 0$ eqs. (140), (141) must be replaced by

$$G_p(r) = G_{pl}(r) \sim \begin{cases} \frac{\phi}{2\pi a^2 r^{d-2}} & , \quad r \lesssim r_c \\ \phi a^{-2} r_c^{2-d} (r/r_c)^{1/\nu-d} & , \; r_c \lesssim r \lesssim \xi \\ -3(4\pi)^{-2}(\tau+\tau^*)^{-2} r^{-2d} e^{-2r/\xi_m} & , \quad r \gtrsim \xi \end{cases} \tag{142}$$

where $\phi = \phi_l$.

The long-range behavior of the magnetic correlation function $G_1(r)$ is analyzed in Appendix C. As follows from eq. (C10), for $n \neq 1$ the magnetic susceptibility $\partial m/\partial h = S_1(0) = \int G_1(r) \mathrm{d}^d r$ is diverging at $h \to 0$:[54]

$$S_1(0) \sim (n-1)\xi^{d-4+\gamma/\nu} \xi_m^{4-d} \propto h^{d/2-2}, \quad h \ll h^*$$

This leads to $m \sim \tau^{\frac{\nu d-\gamma}{2}} \left[1 + \mathrm{const}\,(n-1)(h/h^*)^{d/2-1}\right]$. Note that this singular behavior at $h \to 0$ shows for any $\tau > 0$. Similar singular corrections apply to the concentration of chains $c_l \sim hm$, and to the terminal chain size, N_m:

$$c_l \sim h\tau^{\frac{\nu d-\gamma}{2}} \left[1 + \mathrm{const}\,(n-1)(h/h^*)^{d/2-1}\right]$$

Note that $\partial c_l/\partial h$ does not diverge, but rather shows a weaker singularity at $h \to 0$. [15]

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[15] Of course, $d \geq 2$ is always assumed.

7. Conclusions

1. In this paper we considered the general statistical properties of living equilibrium polymers (solutions and melts), both close to the polymerization transition and far from it. The polymer systems studied generally involve both linear and cyclic chains. The main external parameters (cf. the partition function, eq. (1)) are the activities of a monomer unit (β), of a chain end unit (h) and of a ring (n) controlling, respectively, the total polymer concentration ϕ, the number concentration of linear chains c_l, and the concentration of cyclic chains, ϕ_r. The parameters β and h are continuous: $\beta = e^{\mu}$, where μ is the chemical potential of a monomer unit in k_BT units, and $h^2 = e^{-2E}$, where $2E$ is the chain scission energy. By contrast, n is essentially discrete: $n = 0$ defines the system without rings, $n = 1$ applies to classical living polymers that are allowed to form rings (and whose chemical structure does not distinguish the two directions along the chain), and $n = 2$ corresponds to directional polymers with rings. In all the cases with $n > 0$ and $h \to 0$, only rings are present in the system for $\beta < \beta^*$, while linear chains are formed for $\beta > \beta^*$, where the system is a mixture of rings and infinite chains. The polymerization (for $h \to 0$) occurs at $\beta = \beta^*$ as a thermodynamic second-order phase transition.[1]

The basic critical properties of this transition for $n = 0$, 1 have been established long ago using the polymer-magnetic analogy[45,46,20] allowing to map the living polymer systems to n-component magnetic spin systems. However, the previous studies of living polymers (with $n > 0$) were mainly focussed on the renormalization group calculations of the basic critical exponents[20], while the regions of applicability of the scaling laws were not fully described so far. In this regard, the important parameter is $z^* = b^d/v$ ($d = 3$ is the space dimension), where v is the excluded volume per monomer unit, and b is its typical length. This parameter is large for most polymers, $z^* \gg 1$. (For lattice models $z^* \gg 1$ corresponds to a large number of neighbors that can be connected to a given site.) Two limiting cases were mainly considered for living polymer systems: $z^* \sim 1$ (the critical fluctuation regime), and $z^* \to \infty$ (the mean-field regime). In this study we analyze in detail the effect of large but finite z^* on various statistical properties of living polymers both in the mean-field and fluctuation regimes, in a wide range of external parameters β and h. To this end we employ a convenient polymer-magnetic mapping (cf. the magnetic Hamiltonian, eqs. (5), (B1)) which is different from the model used in the previous studies[20]. The mapping we use, being exact, allows to consider both the critical fluctuation and mean-field regimes in the common framework, which is important as the mean-field behavior is rather typical for the living polymer systems studied experimentally[1].

2. The properties of living polymer systems are analyzed for the general weight of rings, n. We describe the behavior of such living polymers both near and far from the critical polymerization transition point, and we use this opportunity to discuss some fundamental features of their equilibrium polymerization and its analogy with critical phenomena in spin systems highlighting the polymer aspect of this analogy. The main results are explained in terms of polymer physics referring to the polymer chain statistics, the RPA relations for polymer structure factors and the concept of polymer blobs (see Appendices A, D, E).

3. The molecular mass distributions of living linear chains, $c_l(N)$, and living

rings, $c_r(N)$, are obtained in different regimes. We show that in the critical regime of strong fluctuations these distributions are governed by the critical exponents ν_p and γ_p which are generally different (unless $n = 0$) from the magnetic exponents ν and γ. The numerical values of ν_p, γ_p and other exponents are indicated in Table 1. Using these exponents, we developed a simplified physical picture for thermodynamic and correlation properties of the system demonstrating consistency of the basic results (see section 5).

4. Considering living polymer chains with a sense of direction (directional polymers allowing formation of cycles) we found that their equilibrium polymerization falls into a distinct universality class (as compared to the classical living polymers like liquid sulfur[35,20]) corresponding to the O(n) model of magnetism with $n = 2$ (x-y model). This means, apart from qualitatively different correlation properties of the two models (see point 7 below), that all the critical exponents ($\nu, \gamma, \nu_p, \gamma_p$...) involved in the scaling laws describing the behavior of the system near the critical point ($\tau \equiv \mu - \mu^* = 0$, $h = 0$) are different in the two cases, $n = 1$ and $n = 2$. In particular, the polymer osmotic compressibility, $\chi_p = \partial\phi/\partial\tau$, defining the intensity of low-q scattering of concentration fluctuations follow the critical law $\chi_p \propto |\tau|^{-\alpha}$ for small τ, $h = 0$, where $\alpha = 2 - \nu d \approx 0.11$ for $n = 1$, and $\alpha \approx -0.011$ for $n = 2$. Therefore, χ_p diverges at the critical point for classical living polymers, but χ_p remains finite (showing a non-diverging singularity) for directional polymers (see Fig. 5).

5. At the critical point for the polymerization/magnetization transition, $\tau \equiv \mu - \mu^* = 0$, $h = 0$, the system is characterized by just one essential length-scale r_c (apart from the microscopic monomer size b): for $r \ll r_c$ the statistics of polymer segments is Gaussian (the end-to-end distance for a segment of N units is $R(N) \sim bN^{1/2}$), while the segments are swollen for $r \gtrsim r_c$: $R(N) \propto N^{\nu_p}$ for $N > N_c = r_c^2/b^2$. The size $r_c \sim b\,(z^*)^{1/(4-d)}$ can be obtained based on the Ginzburg-Landau Hamiltonian, eq. (B2): r_c is the length-scale separating the regime of nearly Gaussian fluctuations of the field $\varphi(r)$ (for $r \ll r_c$) and the strongly non-Gaussian regime, where the quadratic approximation for H_{GL} fails (for $r \gg r_c$). It is remarkable that r_c is not affected by the rings (it does not depend on n), although the exponent ν_p does depend on n (in fact ν_p decreases with n, see Table 1). Therefore, r_c can be interpreted in terms of the standard polymer theory [50,45]: it marks the transition from Gaussian to swollen segments of an isolated linear polymer chain in solution.

Above the polymerization transition, $\tau > 0$ (where long linear chains are formed), there emerges another length-scale ξ characterizing the concentration fluctuations that diminish significantly at $r \gtrsim \xi$. The correlation length ξ decreases with τ as $\xi \propto \tau^{-\nu}$. The statistics of chains (and their segments) becomes Gaussian again for $r \gg \xi$, with the renormalized statistical segment $b^* = \sqrt{2d}a^*$: $R(N) \sim b^* N^{1/2}$ for large N; $b^* \sim \xi\,(N^*)^{-0.5}$, see eq. (132), where $N^* \propto \tau^{-\phi_g}$ is the number of monomer units in a chain segment of size ξ (the values of the crossover exponent ϕ_g are indicated in Table 1). The scaling regime therefore spans between r_c and ξ in the general case. The two Gaussian regimes ($r \ll r_c$ and $r \gg \xi$) merge when ξ decreases down to r_c at $\tau \sim \tau_c$. The mean-field theory is applicable (and the chain statistics is nearly Gaussian at all length-scales $\gg b$) for $\tau \gg \tau_c$. The crossover parameter τ_c as deduced from the Ginzburg criterion, eq. (106), is $\tau_c \sim (z^*)^{-2/(4-d)}$.

6. An essential part of new results concerns the correlation functions. Among

the different correlation functions, we consider: (i) the function $G_p(r)$ for the total polymer concentration ϕ, (ii) $G_{pl}(r)$ for volume concentration of linear chains, (iii) $G_e(r)$ for concentration of chain ends. At short r, $r \lesssim r_c$, these correlation functions show the mean-field behavior even in the fluctuation regime ($0 < \tau \lesssim \tau_c$): $G_e(r) \simeq h^2/(4\pi a^2 r)$, $G_{pl}(r) \simeq 2\phi_l/(4\pi a^2 r)$, $G_p(r) \simeq (n/2)/(4\pi a^2 r)^2$ for $d = 3$ (cf. eqs. (138), (141), (140)). Moreover, we obtained quantitative predictions, eqs. (58), (E3), (C5), for the correlation functions at $r \gg \xi$, valid both in the fluctuation and mean-field regimes (the latter regime is important as the fluctuation zone is narrow for $z^* \gg 1$). We found that all these functions exhibit long-range power law tails (at $r \gg \xi$) for certain values of the weight of rings, n. This means that the corresponding scattering functions (Fourier transforms of the correlation functions) are singular at $q = 0$ not only at the critical point $\tau = 0$, $h = 0$, but rather on the whole line $\tau > 0$, $h = 0$.

7. Returning to the distinctions between living polymer models with different weights of rings, the present study demonstrates that the systems with $n = 0$, $n = 1$, and $n \geq 2$ show ***qualitatively different*** correlation behaviors both in the fluctuation and mean-field regimes. The differences are not limited to the critical exponents in the fluctuation regime ($r_c \lesssim r \lesssim \xi$): in this regime $G_p(r) = G_{pl}(r) \propto r^{1/\nu - d} \approx r^{-1.3}$, $G_e(r) \propto r^{\gamma/\nu - d} \approx r^{-1.03}$ for $n = 0$; $G_p(r) \propto r^{2/\nu - 2d} \approx r^{-2.83}$, $G_{pl}(r) \propto r^{\phi_g/\nu - d} \approx r^{-1.27}$, $G_e(r) \propto r^{\gamma/\nu - d} \propto r^{-1.03}$ for $n = 1$; and $G_p(r) \propto r^{-3.02}$, $G_{pl}(r) \propto r^{-1.23}$, $G_e(r) \propto r^{-1.04}$ for $n = 2$ ($d = 3$ is assumed here and below). The major qualitative differences concern the behavior of these functions at $r \gg \xi$, where the systems without rings ($n = 0$) show a tail of anti-correlations for the total concentration, $G_p(r) \propto -r^{-2d}$, classical living polymers show an exponential decay, $G_p(r) \propto e^{-r/\xi}$, and directional living polymers show positive long-range correlations, $G_p(r) \propto r^{-2d}$ (see Fig. 6). A similar trend is predicted for the end-correlation function: $G_e(r) \propto -r^{4-2d}$ for $n = 0$, $r \gg \xi$, $G_e(r) \propto e^{-r/\xi}$ for $n = 1$, and $G_e(r) \propto r^{4-2d}$ for $n = 2$. Further, the correlation function $G_{pl}(r) \propto r^{-2d}$ for $n = 0$, but $G_{pl}(r) \propto r^{4-2d}$ for $n = 1, 2$.

8. For $h > 0$ the critical point $\tau = 0$ spreads into a transition zone, $|\tau| \lesssim \tau^*$ of width $\tau^* = \tau^*(h)$, $\tau^*(h) \sim h^{2/3}$ for $h \lesssim \tau_c^{3/2}$, and $\tau^*(h) \propto h^{2/(\nu d + \gamma)}$ for $h \lesssim \tau_c^{3/2}$ (cf. eq. (124)). The linear chains are always finite for $h > 0$, the typical (mean) polymerization index being $N_m \propto 1/h$ for small h. The corresponding chain size $\xi_m \propto 1/\sqrt{h}$ is yet another important length-scale characterizing the living polymer systems with finite scission energy (note that ξ_m is the size, $R(N_m)$, of a linear chain of N_m units). In most cases, the genuine exponential decay of the correlation functions is defined by ξ_m rather than ξ (see eqs. (134), (135), (136), (137), (138), (139), (140), (141), (142)). The dependence of ξ_m on τ and z^* is shown in eq. (131); $\xi_m \gg \xi$ if $\tau^* \ll \tau$ (i.e., for small h, that is, for sufficiently high scission energy $2E$).

Thus, in all the cases ($n = 0, 1, 2...$) the fluctuation region ($0 < \tau \lesssim \tau_c$) is characterized by two essential length-scales: the correlation length ξ and the terminal correlation length $\xi_m \sim \xi(N_m/N^*)^{0.5}$. Within the polymer-magnetic analogy, the length ξ corresponds to the longitudinal fluctuation modes, it diverges at the critical point, $\tau \to 0$, $h \to 0$. The second correlation length ξ_m is associated with soft transverse modes: ξ_m diverges as $h \to 0$ at any $\tau > 0$ (i.e., in the ordered phase). The case $n = 1$ is special, however: here the magnetic Hamiltonian does not involve any massless transverse modes, being a functional of just $\varphi_1(r)$. As a result, for $n = 1$ the length ξ_m does not affect at all the properties related to just

φ_1 including the free energy F (which stays analytical at $h \to 0$), the magnetic correlation function $G_1(r)$, and the polymer end correlation functions $G_e(r)$ and $G_p(r)$: their decay length is $\sim \xi$. By contrast, the correlation functions $G_2(r)$, $F_e(r)$ and $G_{pl}(r)$, whose definition formally involves also the transverse field $\varphi_2(r)$, are characterized by both lengths, ξ and ξ_m, even for $n = 1$, and their genuine decay length is always ξ_m.

9. To sum up, living polymer systems with $z^* \gg 1$ are characterized by the following typical lengths in the fluctuation regime $|\tau| \lesssim \tau_c$: (1) the short-range and long-range statistical segment lengths, $b = \sqrt{2d}a$, $b^* = \sqrt{2d}a^*$, which are non-universal (they depends on the definition of the monomer unit, and increase in the decimation procedure); (2) the mean-field length r_c (polymer segments are always Gaussian for $a \ll r \ll r_c$); (3) the correlation length ξ relevant for many correlation functions; the lengths r_c and ξ define the range of strong fluctuations ($r_c \ll r \ll \xi$), where the correlation functions follow the critical scaling laws; and (4) ξ_m, the terminal correlation length corresponding to the terminal chain size related to the mean polymerization index being $N_m = \xi_m^2/a^{*2}$.

10. In agreement with the classical concepts[45,50], the mean-field theory is essentially applicable in the regimes $r \ll r_c$ and $r \gg \xi$: the chain segments are nearly Gaussian at these length-scales. Accordingly, the fluctuations of the magnetic field, $\delta\varphi$, show nearly Gaussian statistics there. By contrast, for $r_c \lesssim r \lesssim \xi$ the fluctuations are essentially non-Gaussian, and in this sense they are strong. Note, however, that the magnitude of fluctuations always increases at shorter length-scales, so, strictly speaking, the fluctuations $\delta\varphi$ are stronger in the mean-field regime $r \ll r_c$ than in the fluctuation regime $r_c \lesssim r \lesssim \xi$. Therefore, it is not the absolute magnitude, but rather its ratio to the characteristic threshold for the onset of non-Gaussian statistics, that matters. It is also noteworthy that although $\delta\varphi$ fluctuations are Gaussian for $r \ll r_c$, the fluctuations of monomer concentrations (ϕ or ϕ_l) are non-Gaussian in this mean-field regime since these concentrations can not be considered as linear forms of $\delta\varphi$ (rather they correspond to some quadratic functions of $\delta\varphi$).

11. As found in this paper, the dependence of the volume fraction of rings, ϕ_r, on the monomer activity β is non-monotonic (for $n > 0$, $d \leq 3$): ϕ_r increases with β at low β, shows a maximum $\phi_r > \phi^*$ at $\beta < \beta^*$, then ϕ_r decreases at higher β down to the local minimum at the edge of the fluctuation zone (at $\beta/\beta^* - 1 \sim \tau_c$), and finally ϕ_r increases again at $\beta > \beta^*$ outside the fluctuation zone (cf. eq. (130)). The maximum rate of change, $|\partial\phi_r/\partial\beta|$, is predicted near the polymerization transition, at $|\beta/\beta^* - 1| \lesssim \tau^*$, i.e. well inside the region, where ϕ_r decays with β.

12. It was shown[20] that $\phi_l \gg \Delta\phi \equiv \phi - \phi^*$ for classical linear polymers in the fluctuation regime: above the polymerization transition linear chains are formed mainly at the expense of the cyclic chains. We recover this interesting behavior here showing that it stays valid also for the case of directional polymers (where the distinction between the critical τ-exponents for $\Delta\phi$ and ϕ_l is nearly twice stronger, see eqs. (128), (129)). We offer the following qualitative physical explanation of this general feature of living polymers with rings : Exactly at the transition point ($h = 0$, $\phi = \phi^*$, $\tau = 0$, $\phi_l = 0$) there are only cyclic polymers whose length distribution is (cf. eq. (133)):

$$c_r(N) \sim N^{-1}R(N)^{-d}, \quad R(N) \sim N^{\nu_p}, \quad N \gtrsim N_c$$

For simplicity, we disregard the dependence on z^* setting $N_c \sim 1$. At $\tau > 0$ some long linear chains are formed with volume concentration ϕ_l. The presence of linear chains must lead to a decrease of the statistical weight for rings by a factor $1 - \kappa(N)$ resulting in their lower partial concentration: $\Delta c_r(N) = -\kappa(N) c_r(N)$ and to a decrement of their total volume concentration, $\Delta\phi_r < 0$. There are two possibilities: either $\phi_l + \Delta\phi_r \sim \phi_l$ (the total increment of the mass of linear chains and long rings is $\sim \phi_l$), or $\phi_l + \Delta\phi_r \ll \phi_l$. Let us assume the first option. Then, for $N \sim 1$ the decrement factor, $\kappa(N)$, is nearly the fraction of the volume occupied by linear chains: $\kappa(1) \sim \phi_l$. A larger ring (with $N \gg 1$) interacts with N-blobs of linear chains (segments of N monomer units) rather than individual monomers. The blob interaction is strong in the fluctuation regime, so the excluded volume for N-rings is nearly proportional to the volume fraction of the blobs ϕ_b: $\kappa(N) \sim \phi_b$. The latter quantity was estimated in the argument above eq. (69): $\phi_b \sim \phi_l N^{\nu_p d - 1}$ as long as $\phi_b \lesssim 1$, i.e. $1 \lesssim N \lesssim N^* \sim \phi_l^{-1/(\nu_p d - 1)}$. Thus

$$\Delta c_r(N) = -\kappa(N) c_r(N) \sim -\phi_l N^{\nu_p d - 1} c_r(N) \sim -\phi_l N^{-2}$$

hence the decrement of the total volume concentration of rings is

$$\Delta\phi_r = \int N \Delta c_r(N) \mathrm{d}N \sim -\phi_l \int_1^{N^*} N^{-1} \mathrm{d}N \sim -\phi_l \ln N^* \tag{143}$$

This equation shows that $|\Delta\phi_r| \gg \phi_l$ as $N^* \gg 1$. This overcompensation of the linear chain increment by a depletion of the rings points to a negative feedback mechanism keeping the total concentration nearly constant: $\Delta\phi \ll \phi_l$. (Of course, $\Delta\phi = \phi_l + \Delta\phi_r$ must always be positive, as follows from the general thermodynamic condition $\partial\phi/\partial\tau > 0$, so eq. (143) formally yields a contradiction showing that the first option taken above is impossible.) Therefore, the general compensation behavior of rings vs. linear chains comes as a result of their interactions which are enhanced in the fluctuation regime. It is thus predicted for any living system with rings (that is, for any $n > 0$). Formally, this feature is enforced as long as the crossover exponent ϕ_g exceeds 1,[20] which is apparently always true for $n > 0$ (see Table 1).

13. In this paper a considerable attention was given to the correlation function of the total concentration, $G_p(r)$, in particular, to its long-range behavior, which was already considered in our previous studies[31,32]. The known predictions for $G_p(r)$ are generalized here in two directions: for arbitrary n and for $h > 0$ (in particular, we obtained quantitative equation for the terminal decay of G_p at $r \gtrsim \xi_m$, cf. eq. (58)). Moreover, it is revealed that this function shows a long-range tail for $n = 0$ and $n = 2$, but not for $n = 1$. The distinction between polymer systems with $n = 0$ and $n = 1$ was attributed to the fact that the real-space polymer Hamiltonian is non-local for $n = 0$[31,32], but is local for $n = 1$ (classical living polymers). However, it may seem that the Hamiltonian is also local for $n = 2$ (directional living polymers). Indeed, in both cases, $n = 1$ and $n = 2$, the main selection rule for placing the bonds is local: the number of bonds meeting at each site must not exceed 2 (and there is no need to check whether rings are formed or not). This issue is analyzed in Appendix A, where it is shown that the real-space Hamiltonian for directional polymers involves a non-local term.

14. As shown in section 2, the directional living polymers (see Introduction) correspond to $n = 2$. Alternatively, the case $n \geq 2$ can be realized with multi-component mixtures of classical living polymers (the number of components being

n), where each component can form cyclic chains. The main problem here concerns the compatibility of the components. Interestingly, our analysis shows that the presence of both short and long rings enhances the thermodynamic miscibility of the polymer components.

15. To verify the predicted differences in the equilibrium properties of classical and directional living polymers either experimentally or by computer simulations, it would be interesting to focus on (i) The dependence of osmotic compressibility χ_p on chemical potential or concentration (see point 4 above and Fig. 5), and (ii) The behavior of the polymer concentration correlation function $G_p(r)$ on the distance r at $r \gg \xi$ (see point 7 above and Fig. 6). In particular, it would be appropriate to do simulations for the three living polymer models (with $n = 0$, 1, 2 and keeping all other parameters the same), and to try and find the ***differences*** between the correlation functions $G_p(r)$ obtained for all these cases.

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APPENDIX A: Discussion of long-range effects for a real-space model of living polymers

There are no long-range interactions (beyond the correlation length ξ) in classical equilibrium systems involving linear and cyclic chains, but, somewhat surprisingly, these effects reappear in the analogous systems of directional polymers. Although these properties come rather directly from the polymer-magnetic analogy, it is useful to treat the problem also within an explicit real-space model. Here we follow the approach proposed by I. Ya. Erukhimovich.[48]

For simplicity, consider the standard bead-spring model of polymer chains[50]. The aim is to find the free energy $\mathcal{F}$ of a living polymer system for a given overall distribution of monomers with concentration field $c(\underline{r})$: $\mathcal{F} = \mathcal{F}_{conf}\left[c(r)\right] + \mathcal{F}_{int}\left[c(r)\right]$. Here the second term is the free energy of excluded volume interactions of monomer units. Below we focus on the conformational free energy (the first term, $\mathcal{F}_{conf}\left[c(r)\right]$). The interactions are irrelevant for $\mathcal{F}_{conf}$, so it can be calculated for an ideal polymer system.[50] To this end, we take the following route: First, the living polymer system is mapped to a system of dimers by just cutting each internal bead in two halves. Thus, each dimer is a bond (spring) with two half-monomers at its ends. Next we calculate the free energy $\mathcal{F}_d$ of a system of ideal dimers (with concentration $c_e(r) = 2c(r)$ of half-beads), and then find a simple relation between $\mathcal{F}_{conf}$ and $\mathcal{F}_d$.

The polymer free energy (effective Hamiltonian) $\mathcal{F}_{conf}\left[c\right]$ can be defined using the following physical coarse-graining procedure: the system is divided in cells of volume V_1 (such that typically there are many monomers in each cell, $V_1 c \gg 1$), the number of monomers in the ith-cell is fixed at $n_i = c(r_i)V_1$. Then $\mathcal{F}_{conf}[c] = -k_B T \ln Z_{conf}\left\{n_i\right\}$. Here $Z_{conf}\left\{n_i\right\}$ is the partition function of the ideal living polymer system (where both polymer rings and linear chains are allowed) for a given set $\{n_i\}$. (We assume for simplicity that there are no free ends, that is, linear chains are infinite.)

The free energy of the system of dimers, $\mathcal{F}_d = \mathcal{F}_d\,[c_e]$, is defined in a similar way: $\mathcal{F}_d[c_e] = -k_B T \ln Z_d\,\{\nu_i\}$, where $Z_d\,\{\nu_i\}$ is the partition function of the dimer system for a given set $\{\nu_i\}$; $\nu_i = c_e(r_i)V_1 = 2n_i$ is the number of dimer ends in the ith-cell.

There is an obvious relation between the two systems: the polymer system can be obtained from dimers by simple pairwise association of $2n_i$ dimer ends in each cell (yielding n_i pairs = full monomers). The corresponding combinatorial factor is $K(n_i) = (2n_i - 1)!! = (2n_i)!/\left(2^{n_i} n_i!\right)$. Therefore $Z_{conf}\,\{n_i\} = Z_d\,\{\nu_i\}\, V_1^{-\mathcal{N}} \prod_i K(n_i)$, where $\mathcal{N} = \sum_i n_i$ is the total number of monomers. Hence we get the relation ($k_B T$ is considered as the energy unit here and below)

$$\mathcal{F}_{conf}[c] = \mathcal{F}_d\,[c_e] - \int c(r) \ln \frac{2c(r)}{e} \mathrm{d}^3 r$$

The last term in the r.h.s. is explicitly local and non-singular. It therefore remains to find the dimer energy $\mathcal{F}_d$. This can be done by considering the ideal dimers in an external field $\varphi(r)$ conjugate to concentration:

$$Z_d[\varphi] = \int Z_d\,\{\nu_i\}\, e^{-\sum_i \varphi(r_i)\nu_i} \mathcal{D}\,\{\nu_i\} \tag{A1}$$

In the mean-field approximation the integration reduces to evaluation of the maximum of the integrand. This results in $\widetilde{\mathcal{F}}_d\,[\varphi] = -\ln Z_d\,[\varphi]$, which is connected with $\mathcal{F}_d\,[c_e]$ by Legendre transformation:

$$\mathcal{F}_d\,[c_e] \simeq \max_{\varphi} \left\{ \widetilde{\mathcal{F}}_d\,[\varphi] - \int c_e(r)\varphi(r) \mathrm{d}^3 r \right\} \tag{A2}$$

The grand canonical free energy $\widetilde{\mathcal{F}}_d\,[\varphi]$ can be easily calculated as it reduces to that of a single dimer in external field. The resultant $\widetilde{\mathcal{F}}_d\,[\varphi]$ is a local functional, and so is the functional $\mathcal{F}_d\,[c_e]$. Moreover, as the ideal system of dimers obviously does not show any soft modes, the non-mean-field (fluctuation) corrections to eq. (A2) are also local, so that the free energy remains local in the general case. This means that the living polymer system does not show any long-range effects (either correlations or interactions). Importantly, so far we implicitly assumed that the polymers are classical (non-directional), with both directions along the backbone being equivalent.

The situation is entirely different for directional polymers. In this case the reference system of dimers must be directional as well: each dimer must have distinct ends, say white and black, and we must impose the obvious rule that only ends of different color can associate to make a polymer (i.e., white with black). Accordingly, we have to consider two concentrations $c_w(r)$ and $c_b(r)$ for white and black ends, respectively, hence the free energy $\mathcal{F}_d\,[c_w(r), c_b(r)]$ is a functional of the two concentrations. In addition, two external fields, $\varphi_w(r)$ and $\varphi_b(r)$, must be introduced together with the free energy of the dimer system in these fields, $\widetilde{\mathcal{F}}_d\,[\varphi_w(r), \varphi_b(r)]$. As before, the latter free energy $\widetilde{\mathcal{F}}_d\,[\varphi_w(r), \varphi_b(r)]$ can be easily calculated and represented as a local functional. In analogy with eq. (A1) we have:

$$e^{-\widetilde{\mathcal{F}}_d[\varphi_w(r),\varphi_b(r)]} = \int \mathcal{D}\,[c_w(r), c_b(r)]\, e^{-\mathcal{F}_d[c_w(r),c_b(r)] - \mathcal{H}_{\varphi c}} \tag{A3}$$

where $\mathcal{H}_{\varphi c} = \int \left(\varphi_w(r)c_w(r) + \varphi_b(r)c_b(r)\right) \mathrm{d}^3r$. In the mean-field approximation it reduces to

$$\mathcal{F}_d\left[c_w(r), c_b(r)\right] \simeq \max_{\varphi_w, \varphi_b} \left\{ \tilde{\mathcal{F}}_d\left[\varphi_w(r), \varphi_b(r)\right] - \mathcal{H}_{\varphi c} \right\} \tag{A4}$$

Suppose there are n black and n white dimer ends in a V_1-cell. Their association leads to the combinatorial factor $K'(n) = n!$ which is not drastically different from $K(n)$ considered above. The major difference comes from the very restriction that the number of black and white ends ($n_b = c_b(r)V_1$ and $n_w = c_w(r)V_1$) must be exactly equal in each cell:

$$c_w(r) = c_b(r) = c(r) \tag{A5}$$

This difference does not emerge at the mean-field level: the condition (A5) leads to $\varphi_w = \varphi_b$ in eq. (A4), so the mean-field $\mathcal{F}_d$ reduces to that for non-directional dimers. The mean-field free energy $\mathcal{F}_d[c(r), c(r)]$ is therefore purely local. However, the fluctuation correction is important here. An inspection of eq. (A3) reveals that calculation of $\tilde{\mathcal{F}}_d\left[\varphi, \varphi\right]$ involves integration of $e^{-\mathcal{F}_d[c_w(r), c_b(r)]}$ over $\eta(r) = c_w(r) - c_b(r)$ for a fixed $c_w(r) + c_b(r)$. Note that $\eta(r)$ measures the deviation from the imposed condition (A5). It is instructive to expand $\mathcal{F}_d$ as a series in η. Analyzing the dimer system, we get in the quadratic approximation:

$$\Delta\mathcal{F}_d\left[\eta\right] \equiv \mathcal{F}_d\left[c - \eta/2, c + \eta/2\right] - \mathcal{F}_d\left[c, c\right] \sim \int \eta(r)\eta(r') \frac{1}{|r - r'|} \mathrm{d}^3r \mathrm{d}^3r'$$

The free energy increment $\Delta\mathcal{F}_d\left[\eta\right]$ is thus strongly non-local. This feature translates in the non-local fluctuation correction to the mean-field result, eq. (A4). In turn, the non-local energy term brings in long-range correlation/interaction effects in melts and concentrated solutions of directional polymers.

To summarize, a system of symmetric dimers can be rigorously mapped to a system of equilibrium (living) chains and rings, and this mapping justifies the absence of long-range effects in the latter system. By contrast, the similar mapping of a system of asymmetric dimers to a system of directional living polymers involves an essential additional condition stating the balance of inward and outward bonds for each cell and bringing in the long-range effects for the directional polymer systems.

APPENDIX B: Summary on the critical behavior of the O(n) model

The generalized magnetic Hamiltonian used in this paper is $H_m\left[\varphi\right] = H_0\left[\varphi\right] + H_1\left[\varphi\right]$ with (cf. eq. (5))

$$H_0\left[\varphi\right] = \frac{1}{2}\sum_{i,j} K_{i,j}^{-1} \varphi_{\alpha i}\varphi_{\alpha j},$$

$$H_1\left[\varphi\right] = -\sum_i \ln\left(1 + \beta h\varphi_{1i} + \frac{\beta}{2}\left(\varphi_{\alpha i}\varphi_{\alpha i}\left(1 - \frac{g}{n-1}\right) + \frac{ng}{n-1}\varphi_{1i}^2\right)\right) \tag{B1}$$

where $\alpha = 1, 2..n$, and g is the parameter of uniaxial quadratic anisotropy. This Hamiltonian has the same symmetry as the standard O(n) Ginzburg-Landau Hamiltonian[49],

$$H_{GL}[\varphi] = \int \mathrm{d}^d r \left\{ \frac{-\tau}{2}\varphi^2 + \frac{a^2}{2}(\nabla\varphi)^2 - \frac{g}{n-1}\left(n\varphi_1^2 - \varphi^2\right) + \frac{1}{8}\varphi^4 - h\varphi_1 \right\} \tag{B2}$$

where $\varphi^2 = \varphi_\alpha\varphi_\alpha$, $\varphi_\alpha = \varphi_\alpha(r)$, $\alpha = 1..n$, $(\nabla\varphi)^2 = (\nabla_\omega\varphi_\alpha)^2$, $\omega = 1..d$, $\varphi^4 = (\varphi^2)^2$. The two models are nearly equivalent falling in the same universality class and showing the same critical properties.

The parameter h should be identified with magnetic field. For $h = 0$ the model, eq. (B1), shows a continuous magnetization transition at $\beta = \beta^*$, and $\tau = \ln(\beta/\beta^*)$ should be considered as the temperature parameter. The main properties of the standard O(n) model[49] are summarized below for $|\tau| \ll 1$, $h \ll 1$ in terms of the critical exponents ν, γ, ϕ_g (crossover exponent for g) for the space dimension d.

Let us first set $g = 0$. At $\tau > 0$ and $h = 0$ the magnetization $m = \langle\varphi_1\rangle$ is nonzero,

$$m \sim \tau^{(d\nu-\gamma)/2} \tag{B3}$$

and

$$m \sim h^{(d\nu-\gamma)/(d\nu+\gamma)} \tag{B4}$$

for $h > 0$ and $\tau = 0$. For $\tau < 0$

$$m \sim h\,|\tau|^{-\gamma} \tag{B5}$$

The latter equation is valid for $h \ll h^*$, where $h^* \sim |\tau|^{(d\nu+\gamma)/2}$.

The free energy per unit volume (per site) for $h = 0$, $g = 0$ is

$$F_m \simeq -\text{const}\ |\tau|^{\nu d} + F_{reg}$$

where the first term accounts for the dominant singularity at $\tau = 0$, and F_{reg} is a more regular part. Thus,

$$\left\langle\varphi^2\right\rangle \sim -\partial F_m/\partial\tau \sim \text{const}\ + |\tau|^{d\nu-1}\,\mathrm{sgn}(\tau) \tag{B6}$$

so the heat capacity is

$$C \sim \partial\left\langle\varphi^2\right\rangle/\partial\tau \sim -\partial^2 F_m/\partial\tau^2 \sim \text{const}\ + |\tau|^{d\nu-2} \tag{B7}$$

More precisely, for $\tau \neq 0$

$$F_m = -\,|\tau|^{\nu d} f_\pm(h/h^*, g/g^*) + F_{reg} \tag{B8}$$

where '+' or '-' correspond to sgn(τ), $g^* \sim |\tau|^{\phi_g}$ is the characteristic magnetic anisotropy. In particular,

$$f_+(x,y) \sim 1 + C_1 x + C_2 y, \quad f_-(x,y) \sim 1 + C_1 x^2(1 + C'y) \tag{B9}$$

for $x = h/h^* \ll 1$, $y = g/g^* \ll 1$, where C_1, C_2, C' are generic positive constants. The behavior of $f_\pm$ for $x \gg 1$ can be found demanding that $F_m = F_m(\tau, h, g)$ is nearly independent of τ in this regime of high h:

$$f_{\pm}(x,y) \sim x^{2d\nu/(d\nu+\gamma)}\left(1 + C'yx^{-2\phi_g/(d\nu+\gamma)}\right), \quad x \gg 1, \;\; y \ll 1 \tag{B10}$$

Note that the scaling laws for m follow from eqs. (B9), (B10) since $m \sim -\partial F_m/\partial h$. Further, $\langle \varphi_1^2 - \varphi_2^2 \rangle \sim -\frac{\partial F_m}{\partial g}$, so we get for $g \to 0$ and $|\tau| \ll 1$:

$$\left\langle \varphi_1^2 - \varphi_2^2 \right\rangle \sim -\frac{\partial F_m}{\partial g} \sim \tau^{\nu d - \phi_g}, \;\; \tau > 0, \;\; h \ll h^*, \tag{B11}$$

$$-\frac{\partial F_m}{\partial g} \sim h^2 \left|\tau\right|^{-\gamma-\phi_g}, \;\; \tau < 0, \;\; h \ll h^* \tag{B12}$$

and

$$-\frac{\partial F_m}{\partial g} \sim h^{2(\nu d - \phi_g)/(d\nu+\gamma)}, \quad h \gg h^* \tag{B13}$$

The numerical results[51–53] for the main critical exponents for $d = 3$ are summarized in Table 1.

Below we assume no quadratic anisotropy, $g = 0$. The most essential length-scale in the critical region is the correlation length ξ defining the maximum size of the regions with strong and non-Gaussian fluctuations of the field $\varphi(r)$:

$$\xi \sim \begin{cases} |\tau|^{-\nu}, & h \ll h^* \\ h^{-2\nu/(d\nu+\gamma)}, & h \gg h^* \end{cases} \tag{B14}$$

For $n = 1$ (Ising model) the correlation function $G_1(r) = \langle \varphi_1(0)\varphi_1(r) \rangle_c$ describes fluctuations of the only field component $\varphi_1(r)$:

$$G_1(r) \sim \begin{cases} r^{\gamma/\nu - d}, & 1 \ll r \ll \xi \\ \xi^{\gamma/\nu - d}(r/\xi)^{2-d}\exp(-r/\xi), & r \gg \xi \end{cases} \tag{B15}$$

The Fourier transform of $G_1(r)$ is

$$S_1(q) \sim \begin{cases} q^{-\gamma/\nu}, & 1 \gg q \gg 1/\xi \\ \xi^{\gamma/\nu}\left(1 + q^2\xi^2\right)^{-1}, & q\xi \ll 1 \end{cases}$$

The correlation properties are significantly different for $n \neq 1$. In this case we define the transverse correlation function $G_2(r) = \langle \varphi_2(0)\varphi_2(r) \rangle$ in addition to the longitudinal function $G_1(r)$. The soft transverse modes are important as they become massless in the limit $h \to 0$. These modes are characterized by the second (terminal) correlation length ξ_m,

$$\xi_m \sim \begin{cases} h^{-0.5}\tau^{(d\nu+\gamma)/4-\nu} & , \;\; h \ll h^*, \;\; \tau > 0 \\ \xi & , \;\; h \gg h^* \text{ or } \tau < 0 \end{cases} \tag{B16}$$

$\xi_m \gg \xi$ in the ordered state for $h \ll h^*$; $\xi_m \to \infty$ for $h \to 0$. The transverse correlation function $G_2(r)$ shows a power-law decay between ξ and ξ_m:

$$G_2(r) \sim \begin{cases} r^{\gamma/\nu - d}, & 1 \ll r \ll \xi \\ \xi^{\gamma/\nu - d}(r/\xi)^{2-d}e^{-r/\xi_m}, & r \gg \xi \end{cases} \tag{B17}$$

Its Fourier image is

$$S_2(q) \sim \begin{cases} q^{-\gamma/\nu}, \quad 1 \gg q \gg 1/\xi \\ \xi^{\gamma/\nu}\left(1 + q^2\xi_m^2\right)^{-1}, \quad q\xi \ll 1 \end{cases}$$

The longitudinal function $G_1(r)$ shows a different behavior at large distances associated with $G_2(r)$:

$$G_1(r) \sim \begin{cases} r^{\gamma/\nu - d}, \quad 1 \ll r \ll \xi \\ (n-1)\xi^{-\gamma/\nu + d} G_2(r)^2, \quad r \gg \xi \end{cases} \tag{B18}$$

The second line of eq. (B18) is derived in Appendix C. Thus, $G_1(r)$ is characterized by a power-law (rather than exponential) decay beyond $r \sim \xi$: $G_1(r) \propto r^{4-2d}$ for $\xi < r < \xi_m$. The two correlation functions are always similar at short distances, $G_1(r) \sim G_2(r)$ for $r \ll \xi$. Note also that $G_1(\xi) \sim G_2(\xi) \sim m^2$ for $\tau > 0$.

APPENDIX C: Correlation function of longitudinal modes

Below we show that the longitudinal correlation function $G_1(r)$ exhibits a power-law decay for $\tau > 0$, $h = 0$ and $n \neq 1$. We first consider this function in the mean-field regime for $d = 3$ using the effective magnetic Hamiltonian, eq. (46), appropriate at length-scales larger than b. Then we use exactly the same idea as in section 4. There is no need to change variables, rather we just expand H_m as a series in $\delta\varphi_\alpha = \varphi_\alpha - \varphi_\alpha^*$, where $\varphi_\alpha^* = m\delta_{\alpha 1}$ corresponds to the minimum of H_m (m is defined in eq. (7), $m^2/2 \simeq \phi$). Thus, we get $H_m = H_2 + H_3$, where

$$H_2 = \frac{1}{2}\int \left[2\phi\left(\delta\varphi_1\right)^2 + a^2\left(\nabla\varphi\right)^2\right] \mathrm{d}^d r$$

and H_3 includes all higher-order terms:

$$H_3 = \int \left[\frac{1}{2} m\delta\varphi_1\left(\delta\varphi\right)^2 + ...\right] \mathrm{d}^d r$$

(only the most important cubic term is shown above). With H_2 only we get the mean-field functions (cf. eqs. (26), (30))

$$G_{2mf}(r) = \left\langle \varphi_2(0)\varphi_2(r)\right\rangle_{H2} \simeq \frac{1}{4\pi a^2 r} e^{-r/\xi_m}, \quad r \gg b \tag{C1}$$

$$G_{1mf}(r) = \left\langle \delta\varphi_1(0)\delta\varphi_1(r)\right\rangle_{H2} \simeq \frac{1}{4\pi a^2 r} e^{-r/\xi}, \quad r \gg b$$

where $\xi_m \simeq a\sqrt{N_m}$ is the terminal coil size, $N_m \simeq \sqrt{2\phi}/h$ and $\xi \simeq a/\sqrt{2\phi}$. The main correction to the latter result for $r \gg \xi$, $G_{1lr}(r)$, comes from H_3:

$$G_1(r) \simeq G_{1mf}(r) + G_{1lr}(r), \tag{C2}$$

$$G_{1lr}(r) \simeq \left\langle \delta\varphi_1(0)\delta\varphi_1(r) H_3^2/2\right\rangle_{H2}$$

More explicitly (cf. eq. (50)),

$$G_{1lr}(r) \simeq \frac{m^2}{8}\left\langle \delta\varphi_1(0)\delta\varphi_1(r)\int \delta\varphi_1(r')\left(\delta\varphi_\alpha(r')\right)^2 \mathrm{d}^d r' \int \delta\varphi_1(r'')\left(\delta\varphi_\beta(r'')\right)^2 \mathrm{d}^d r''\right\rangle_{H2}$$

On using the Wick's theorem, it is clear that the integrals in the r.h.s. are dominated by the regions $r' \approx 0$, $r'' \approx r$ or $r' \approx r$, $r'' \approx 0$:

$$G_{1lr}(r) \simeq \frac{m^2}{8} 4\chi_{mf}^2(n-1)G_2(r)^2$$

where

$$\chi_{mf} = \int G_{1mf}(r)\mathrm{d}^d r = S_{1mf}(0) \simeq 1/(2\phi)$$

Thus

$$G_{1lr}(r) \simeq \frac{n-1}{4\phi}\left(\frac{1}{4\pi a^2 r}\right)^2 e^{-2r/\xi_m}, \quad r \gg b \tag{C3}$$

For $r \gg \xi$ the first term in eq. (C2) can be neglected, so $G_1(r) \simeq G_{1lr}(r)$. The end-correlation function $G_e(r) \simeq h^2 G_1(r) \simeq \frac{2\phi}{N_m^2}G_1(r)$, cf. eqs. (42), so

$$G_e(r) \simeq \frac{1}{2}\frac{n-1}{N_m^2}\left(\frac{1}{4\pi a^2 r}\right)^2 e^{-2r/\xi_m}, \quad r \gg \xi, \quad d=3 \tag{C4}$$

Although this result was derived in the mean-field regime, it stays essentially valid also in the critical regime, provided that the parameter a is renormalized: $a \to a^*$ (cf. eqs. (79), (132)). In the general case the terminal length is $\xi_m \simeq a^*\sqrt{N_m}$ (cf. (57)), hence

$$G_e(r) \simeq \frac{1}{2}\frac{n-1}{\xi_m^4}\left(\frac{1}{4\pi r}\right)^2 e^{-2r/\xi_m}, \quad r \gg \xi, \quad d=3 \tag{C5}$$

Eq. (C5) can be obtained noting that $G_e(r)$ according to its physical meaning must be invariant with respect to a decimation procedure (grouping of monomer units)[45]. Therefore, G_e may depend on just two dimensional parameters, the concentration of ends $2\phi/N_m$ and ξ_m. Noting also that $G_e(r) \propto N_m^{-2} r^{4-2d}$ is the general scaling behavior for $\xi \ll r \ll \xi_m$, we get $G_e(r) \propto \xi_m^{-4}$, which leads to eq. (C5).

The argument does not change in the case of arbitrary d. The general result is

$$G_e(r) \simeq \frac{1}{2}\frac{n-1}{\xi_m^4}G(r,\xi_m)^2, \quad r \gg \xi \tag{C6}$$

where

$$G(r,\xi) \equiv \int_q \left(q^2 + \xi^{-2}\right)^{-1} e^{\mathrm{i}q\cdot r}, \tag{C7}$$

$$G(r,\xi) = \frac{1}{4\pi r}e^{-r/\xi}, \quad d=3, \tag{C8}$$

$$G(r,\xi) \simeq A_d r^{2-d}, \quad r \ll \xi, \quad A_d = \Gamma(d/2-1)\pi^{-d/2}/4 \tag{C9}$$

Based on the obtained results for G_e we can predict the long-range behavior of $G_1(r)$ in the general case for $\tau > 0$, $h \ll h^*$. Recalling that $G_1(r) \simeq G_e(r)/h^2$ for $z^* \gg 1$, we get the general result (cf. eqs. (42), (43)):

$$G_1(r) \simeq \frac{n-1}{2} m^2 \left(2\phi_l\right)^{-2} \left(a^*\right)^{-4} G(r, \xi_m)^2, \quad r \gg \xi \tag{C10}$$

In the mean-field regime for $d = 3$ the above equation agrees with eq. (C3). Thus, $G_1(r) \sim (n-1)\xi^{d+\gamma/\nu-4} r^{4-2d} e^{-2r/\xi_m}$, $r \gg \xi$, in agreement with the second line of eq. (B18). In particular, for $h = 0$, $\tau > 0$ the function $G_1(r)$ follows the long-range power-law, $G_1(r) \propto r^{4-2d}$, if $n \neq 1$. At $r \sim \xi$ the function $G_1(r)$, eq. (C10), matches the short-range asymptotics, $G_1 \sim r^{\gamma/\nu-d}$. The general long-range behavior for the functions $F_e(r)$, $G_2(r)$ can be found in a similar way based on eq. (C1):

$$F_e(r) \simeq \frac{2c_l}{\xi_m^2} G(r, \xi_m), \quad r \gg \xi, \tag{C11}$$

$$G_2(r) \simeq \frac{m^2}{2\phi_l} \left(a^*\right)^{-2} G(r, \xi_m), \quad r \gg \xi \tag{C12}$$

in agreement with the second line of eq. (B17).

APPENDIX D: The short-range behavior of $G_p(r)$

For $n > 0$ the basic mean-field prediction for $G_p(r)$ (defined in eq. (49)) becomes invalid at short r, for $r \lesssim \tilde{r} \ll \xi$. To predict $G_p(r)$ for $r \lesssim \tilde{r}$ it is instructive to resort to the real-space polymer model. The new short-range regime has a clear physical meaning within this framework: for $r \lesssim \tilde{r}$ the fluctuations of the total concentration are dominated by the contribution of polymer rings. To see this we recall that effective interactions of rings are weak in the mean-field regime, hence the rings are almost uncorrelated and can be considered as an ideal-gas system. Therefore, the correlation function of rings, $G_{pr}(r) = \left\langle \phi_r(0)\phi_r(r)\right\rangle_c$, where $\phi_r(r)$ is the local concentration of monomer units belonging to rings, is dominated by the intra-ring correlations:

$$G_{pr}(r) \simeq \int c_r(N) F_r(r, N) \mathrm{d}N$$

where the function $F_r(r, N)$ accounts for monomer correlations inside a ring of N units (the Fourier transform of $F_r(r, N)$ is the formfactor of an N-ring). The mass distribution of rings is defined in eq. (114): $c_r(N) \simeq \frac{n}{2}\frac{1}{N}\left(4\pi N a^2\right)^{-d/2} e^{-N/N_m}$. By virtue of the Gaussian statistics[50]

$$F_r(r, N) \simeq N \left(4\pi N a^2\right)^{d/2} \int_0^N P(r, N_1) P(r, N - N_1) \mathrm{d}N_1 \tag{D1}$$

where $P(r, N)$ is defined in eq. (80) with a^* replaced by a.

Thus, the correlation function $G_{pr}(r)$ is

$$G_{pr}(r) \simeq \frac{n}{2} \left(\frac{1}{a^2} G(r, \xi_m)\right)^2 \simeq (n/2) A_d^2 a^{-4} r^{4-2d}, \quad r \gg a$$

where the function $G(r,\xi_m)$ and A_d are defined in eqs. (C7), (C9). The analogous function for linear chains, $G_{pl}(r)$ (see section 5.3), is defined in the basic mean-field approximation:

$$G_{pl}(r) \simeq 2\phi_l a^{-2} G(r,\xi) \sim \phi_l a^{-2} r^{2-d} e^{-r/\xi}, \quad r \lesssim \xi$$

(cf. eq. (49); for simplicity we assume here that $\phi_l \ll 1$). Using the RPA relation for the polymer structure factor[45]

$$1/S_p(q) \simeq 1/\left[S_{pl}(q) + S_{pr}(q)\right] + v^*$$

($S_{pl}(q)$, $S_{pr}(q)$ are d-dimensional Fourier transforms of the functions $G_{pl}(r)$, $G_{pr}(r)$) we finally get the polymer concentration correlation function, $G_{mf}(r) = \int_q S_p(q) e^{\mathrm{i}q\cdot r}$, for short r:

$$G_{mf}(r) \simeq G_{pl}(r) + G_{pr}(r), \quad r \lesssim \xi$$

Thus,

$$G_{mf}(r) \simeq 2\phi_l a^{-2} G(r,\xi) + (n/2) A_d^2 a^{-4} r^{4-2d}, \quad r \lesssim \xi \tag{D2}$$

in complete agreement with eq. (60).

APPENDIX E: The long-range behavior of $G_{pl}(r)$

Let us consider the correlation function of monomers on linear chains, $G_{pl}(r)$, first, employing the magnetic analogy in the mean-field regime. In analogy with eq. (35) we have (for small $h \ll h^*$)

$$G_{pl}(r) \simeq \langle \rho(0)\rho(r) \rangle_c \tag{E1}$$

where

$$\rho = \frac{1}{2/\beta + \varphi^2}\left(\varphi_1^2 - k\varphi_2^2 - k'\varphi_3^2\right) \simeq \frac{1}{2}\left(\varphi_1^2 - k\varphi_2^2 - k'\varphi_3^2\right) \tag{E2}$$

The last approximation $\frac{1}{2/\beta+\varphi^2} \simeq \frac{1}{2}$ is valid for $z^* \gg 1$ and $\beta > 1$, i.e., above the magnetization transition (it is true also in the critical fluctuation regime, where $\beta \approx \beta^* \simeq 1$, and $\varphi^2 \ll 1$). The fields φ_2 and φ_3 involved in eq. (E2) are two different transverse components of the order parameter. The constants k and k' must satisfy

$$k + k' = 1, \quad k^2 + k'^2 = -1$$

Note that, $\langle \rho \rangle \simeq \phi_l$. In the mean-field regime $\varphi_1 = m + \delta\varphi_1$, $m^2 \simeq 2\phi_l$ (cf. eqs. (7), (9)). Thus, using eq. (E1) the function $G_{pl}(r)$ can be expressed in terms of magnetic correlation functions $G_1(r)$, $G_2(r)$:

$$G_{pl}(r) \simeq 2\phi_l G_{1mf}(r) + \frac{n}{2} G_{2mf}(r)^2, \quad r \gg \xi$$

The function G_{1mf} is small for $r \gg \xi$; on neglecting it we get (for $n > 0$):

$$G_{pl}(r) \simeq \frac{n}{2} G_{2mf}(r)^2 \simeq \frac{n}{2} a^{-4} G(r,\xi_m)^2, \quad r \gg \xi$$

To generalize this result beyond the mean-field regime we use the trick introduced in Appendix C: it is enough to just renormalize the parameter a (cf. the text between eqs. (C4), (C5)):

$$G_{pl}(r) \simeq \frac{n}{2} \left(a^*\right)^{-4} G(r,\xi_m)^2, \quad r \gg \xi \tag{E3}$$

This equation is valid also in the fluctuation zone, for $0 < \tau \lesssim \tau_c$.

Below we provide an alternative derivation of the above equation directly based on the real-space polymer model. First we note that the function $G_{pl}(r)$ for $r \gg \xi$ is much higher than G_p (as can be verified based on the final result, eq. (E3), and eq. (56)): the concentration of black units (belonging to linear chains) fluctuates much stronger than the total concentration. The latter fluctuations can be therefore neglected assuming $\phi = \phi(\underline{r}) = \text{const}$, hence $\phi_l(r) = \text{const} - \phi_r(r)$ and thus G_{pl} is defined by the fluctuations of the concentration ϕ_r of white units: $G_{pl}(r) \simeq G_{pr}(r) = \langle \phi_r(0)\phi_r(r)\rangle - \phi_r^2$. The latter correlation function is mainly due to large rings of size $\gtrsim r$. The volume fraction of such large rings (with $r \gg \xi$) is small compared to the volume fraction of long linear chains (as can be deduced from eqs. (89), (71)), so the effective interactions between these rings are nearly completely screened by the linear chains. Hence, the ring segments (of size $r \gg \xi$) follow the Gaussian statistics, and the rings are almost uncorrelated: it is fair to consider the system as a nearly ideal gas of large rings.

Thus, $G_{pr}(r)$ is dominated by the intra-ring correlations:

$$G_{pr}(r) \simeq \int c_r(N) F_r(r,N) \mathrm{d}N \tag{E4}$$

where the intra-ring correlation function $F_r(r,N)$ is defined in eq. (D1). By virtue of the Gaussian statistics[50] the molecular length distribution of rings is

$$c_r(N) \simeq \frac{n}{2} \frac{1}{N} \left(4\pi N a^{*2}\right)^{-d/2} e^{-N/N_m}$$

(cf. eq. (133) with $R(N) \sim a^* \sqrt{N}$). Using eq. (E4) we get

$$G_{pr}(r) \simeq \frac{n}{2} \left(a^*\right)^{-4} G(r,\xi_m)^2, \quad r \gg \xi$$

where $\xi_m \simeq a^* \sqrt{N_m}$. The above equation defines $G_{pl}(r) \simeq G_{pr}(r)$ which is identical to eq. (E3).

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TABLES

TABLE I. The critical exponents for the O(n) model, $d = 3$, obtained in refs.[51–53], and the corresponding polymer exponents, ν_p, γ_p.

n	ν	γ	$\alpha = 2 - d\nu$	ϕ_g	$\nu_p = \nu/\phi_g$	$\gamma_p = \gamma/\phi_g$
0	0.588	1.1604	0.236	1	0.588	1.160
1	0.6303	1.2403	0.11	1.092	0.577	1.136
2	0.6704	1.3164	-0.01	1.184	0.566	1.112
∞	1	2	-1	2	0.5	1

FIGURE CAPTIONS

FIG. 1. The simplest peptides showing the directional chain structure: (a) achiral polyglycine; (b) D-polyalanine, which is both chiral and isotactic.

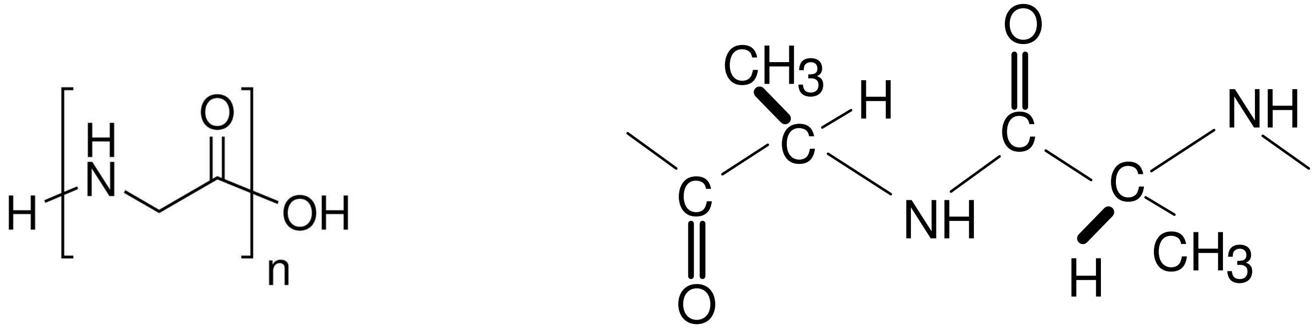
FIG. 2. Head-to-tail supramolecular self-assembly of polar units.

FIG. 3. An example of an asymmetric unit for supramolecular polymerization based on triple H-bonds (dotted lines); R is an alkyl tail. (Cp. with Fig. 11 of ref.[5]).

FIG. 4. The lattice polymer model: $\mathcal{N} = 16$, $\mathcal{N}_m = 12$, $\mathcal{N}_l = 2$, $\mathcal{N}_r = 1$; the monomer concentration $\phi = 12/16 = 0.75$, number concentration of linear chains $c_l = 2/16$. Volume concentration of linear and cyclic chains are $\phi_l = 8/16 = 0.5$, $\phi_r = 4/16 = 0.25$.

FIG. 5. The schematic dependences of the polymer osmotic compressibility χ_p on the monomer chemical potential μ ($\tau = \mu - \mu^*$) for classical living polymers with rings (curve 1 showing singularity $\sim|\tau|^{-0.11}$) and for directional living polymers (curve 2, much weaker singularity).

FIG. 6. The schematic plots of the polymer concentration correlation functions $G_p(r)$ for 3 models: living polymers with no rings (curve 0), classical living polymers with rings (curve 1) and directional living polymers (curve 2).



(a)

(b)

Fig. 1.

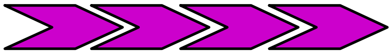


Fig. 2.

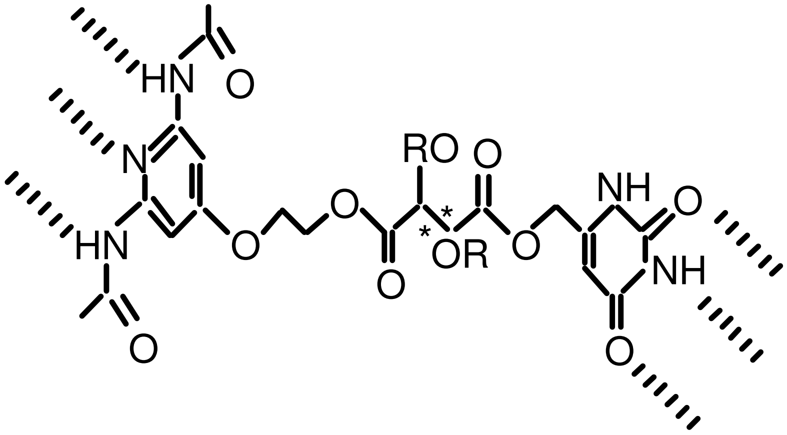


Fig. 3.

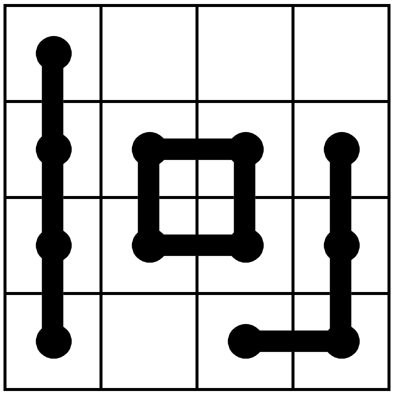


Fig. 4.

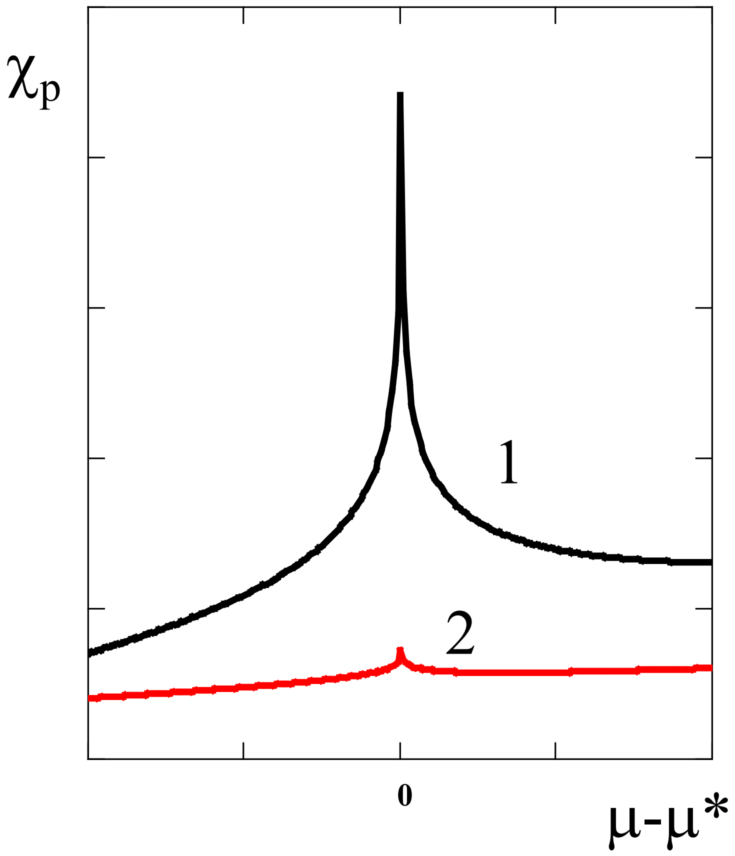


Fig. 5.

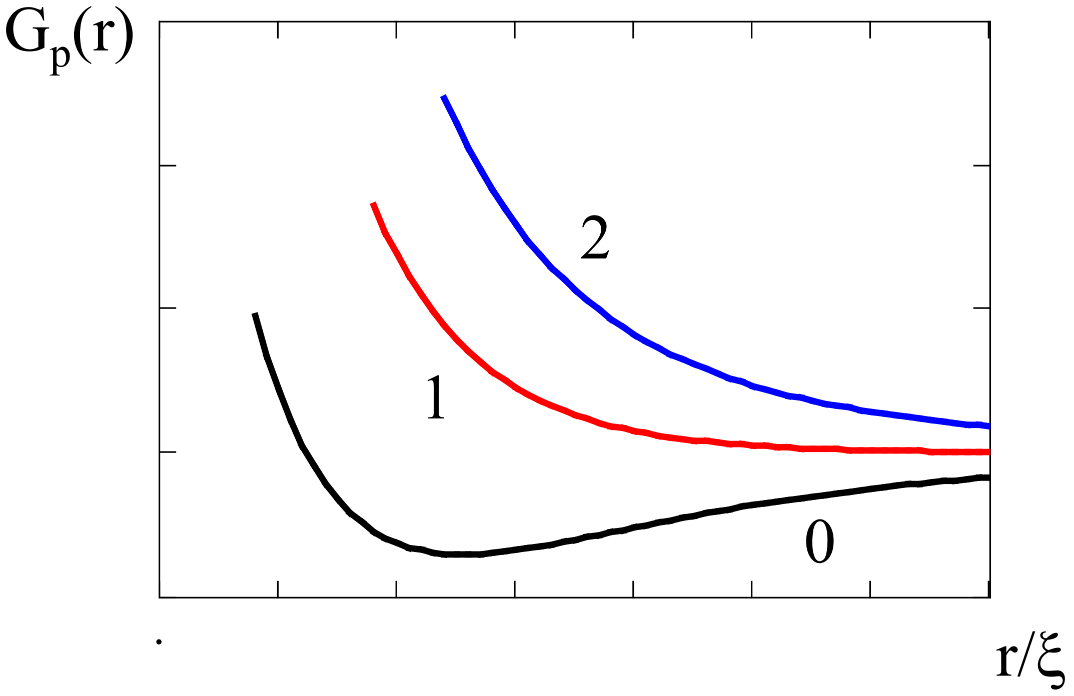
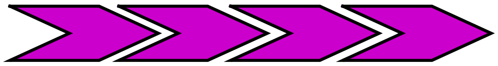


Fig. 6.

TOC entry



Directional living polymers constitute a new universality class with distinct critical and correlation properties