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LETTER TO THE EDITOR

Mean-field theory of polymer melting

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Abstract. We study the Flory model for the melting of a semiflexible polymer chain on a lattice. Using a field theoretical representation of the partition function, we propose a new mean-field theory. Within this theory, the system undergoes a first-order transition at temperature T_c , between a liquid-like phase at temperature $T > T_c$ and an ordered (almost stretched) phase at $T < T_c$, in agreement with the original Flory idea. In addition, we find a disorder point T_D ($> T_c$), separating two liquid phases with different short-range correlations. For $T > T_D$, the short-range correlations are isotropic, whereas for $T < T_D$, one-dimensional short-range order sets in. This disorder point may be relevant to the glass transition.

The statistical mechanics of long, semiflexible, dense self-avoiding polymer chains has been a long-standing controversial problem [1]. It is used to model the melting transition that occurs in polymer systems [2].

Flory has suggested [2] that under increasing stiffness there should be a first-order transition from a melted to a crystalline state. This has been disputed [3, 4] on the basis of certain exactly soluble models for polymers, which have continuous transitions, and it has been shown rigorously [5, 6] that a certain aspect of Flory mean-field theory, namely the existence of a completely frozen crystalline state, is incorrect. Baumgärtner and Yoon [7] have performed Monte Carlo calculations for a model system on a finite lattice and found results corroborating Flory theory. A transfer matrix study of the model in 2D by Saleur [8], shows the existence of a continuous transition from a massless (critical) high-temperature phase to a partially ordered phase, in contradiction with the results of [7]. In a more recent calculation [9] Baumgärtner reached the conclusion that intramolecular interactions alone do not lead to a phase transition.

In this letter, we propose a mean-field theory for the polymer melting problem. This theory applies in high enough dimensions, and should not be taken too quantitatively in $d = 2$.

First, we present a field theoretical representation of the model, from which we get simple upper and lower bounds. By performing the saddle-point method (SPM) on the functional integral, we obtain an isotropic mean-field theory which gives very good results, but corrections to mean-field are large at low temperature and spoil this result. We take this as an indication that the starting point of our expansion is inadequate, and so we propose an anisotropic mean-field theory. This new mean-field gives results very close to the previous one: the theory resembles qualitatively the theory of Flory, with an inactive low-temperature phase, but with a much lower free energy. First-order corrections have been performed in the low-temperature phase, leading to a weak temperature dependence, in agreement with [5] and [6].

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In summary, the system displays a first-order phase transition between a low-temperature one-dimensionally ordered phase (with weak temperature dependence) and a high-temperature liquid-like phase.

In addition, in the liquid phase, we find a disorder point at temperature $T_D > T_c$; this point is the boundary between two liquids: one with isotropic short-range correlations ($T > T_D$) and one with anisotropic (one-dimensional-like) short-range correlations ($T < T_D$). A preliminary account of these mean-field methods can be found in [11].

We consider a d -dimensional hypercubic lattice of $N = L^d$ sites, with periodic boundary conditions, and its associated Hamiltonian paths. We recall that a Hamiltonian path visits all sites of the lattice once and only once (see figure 1). Hamiltonian paths have often been used to model collapsed polymer globules [12]. To mimic the flexibility of the chain, we attribute an energy loss ϵ when two consecutive monomers are not aligned, that is whenever the Hamiltonian path makes a turn (corner). For simplicity, we consider closed paths, but, as is well known in polymer theory [12], boundary conditions play a role only in subdominant terms of the free energy. The partition function of the system, at inverse temperature $\beta = 1/T$, reads

$$\mathcal{Z} = \sum_{\{\mathcal{H}\}} e^{-\beta \epsilon N_c(\mathcal{H})} \quad (1)$$

where $\{\mathcal{H}\}$ denotes the ensemble of all Hamiltonian paths, and $N_c(\mathcal{H})$ denotes the number of corners present in path \mathcal{H} .

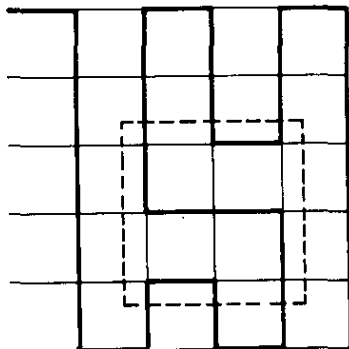


Figure 1. A Hamiltonian path on a square lattice. Inside the dashed square is shown the lowest energy excitation of the fully stretched configuration, with six corners.

In order to perform calculations, we use a technique, presented in [13], which yielded excellent results in the enumeration of non-weighted Hamiltonian paths.

We start from the following identity:

$$\mathcal{Z} = \lim_{n \rightarrow 0} \frac{1}{n} \frac{\int \prod_{\alpha=1}^d d\varphi_{\alpha}(\mathbf{r}) e^{-A_G} \prod_{\mathbf{r}} (\sum_{\alpha} \frac{1}{2} \varphi_{\alpha}^2(\mathbf{r}) + e^{-\beta \epsilon} \sum_{\alpha < \omega} \varphi_{\alpha}(\mathbf{r}) \cdot \varphi_{\beta}(\mathbf{r}))}{\int \prod_{\alpha=1}^d d\varphi_{\alpha}(\mathbf{r}) e^{-A_G}} \quad (2a)$$

with

$$A_G = \frac{1}{2} \sum_{\alpha=1}^d \sum_{\mathbf{r}, \mathbf{r}'} \varphi_{\alpha}(\mathbf{r}) (\Delta_{\mathbf{r}\mathbf{r}'}^{\alpha})^{-1} \varphi_{\alpha}(\mathbf{r}') \quad (2b)$$

where $\varphi_{\alpha}(\mathbf{r})$ is an n -component real field defined in each direction $\alpha = 1, \dots, d$, attached to all points \mathbf{r} of the lattice. The operator $\Delta_{\mathbf{r}\mathbf{r}'}^{\alpha}$, is 1 if \mathbf{r} and \mathbf{r}' are nearest

neighbours in direction α , and 0 otherwise, and $(\Delta_{rr}^\alpha)^{-1}$ denotes its inverse. The expression (2) is $O(n)$ invariant. To prove the identity (2), we make use of Wick's theorem. At each site of the lattice, one must choose either a term of the form $\frac{1}{2}\varphi_\alpha^2(r)$ or of the form $e^{-\beta\epsilon}\varphi_\alpha(r) \cdot \varphi_\beta(r)$. The first term will be seen as describing a path going through r in direction α without turning, whereas the second one assigns a weight $e^{-\beta\epsilon}$ to a path turning from direction α to β at point r . The propagator of the field $\varphi_\alpha(r)$ is Δ_{rr}^α and thus, the elementary contraction is given by:

$$\overline{\varphi_\alpha^u(r)\varphi_\beta^v(r')} = \delta_{\alpha\beta}\delta_{uv}\Delta_{rr}^\alpha \tag{3}$$

where u and v denote any of the n components of the fields $\varphi_\alpha(r)$. According to Wick's theorem, we must contract all fields $\varphi_\alpha(r)$ using (3). Thus, the result is a sum over all possible Hamiltonian paths, connected or not, covering the whole lattice, with a weight $e^{-\beta\epsilon}$ at each turn. Further, since the propagator conserves the index u of component of the field, the summation over the component index u yields a factor n for each connected part of the paths. The term proportional to n thus yields the contribution of all connected paths, and in order to extract it, it is customary [14] to take the limit $n \rightarrow 0$.

Rewriting the product in (2a) as

$$\frac{1}{2}(1 - e^{-\beta\epsilon}) \sum_{\alpha=1}^d \varphi_\alpha^2(r) + \frac{1}{2}e^{-\beta\epsilon} \left(\sum_{\alpha=1}^d \varphi_\alpha(r) \right)^2 \tag{4a}$$

and using the Schwartz inequality

$$\frac{1}{d} \sum_{\alpha=1}^d \varphi_\alpha^2(r) \geq \left(\frac{1}{d} \sum_{\alpha} \varphi_\alpha(r) \right)^2 \tag{4b}$$

we get

$$\left(\frac{q(\beta)}{2d} \right)^N \int e^{-A_G} \prod_r \left[\frac{1}{2} \left(\sum_{\alpha} \varphi_\alpha(r) \right)^2 \right] \leq \mathcal{Z} \leq \left(\frac{q(\beta)}{2} \right)^N \int e^{-A_G} \prod_r \left(\frac{1}{2} \sum_{\alpha} \varphi_\alpha^2(r) \right) \tag{4c}$$

where

$$q(\beta) = 2(1 + (d-1)e^{-\beta\epsilon}) \tag{5}$$

is an effective coordination number.

This in turn yields

$$-T \log \left(\frac{q(\beta)}{2} \right) \leq F \leq \min \left(0, -T \log \left(\frac{q(\beta)}{e} \right) \right) \tag{6}$$

where F is the free energy per monomer and $e = 2.71828$.

As in [13], we evaluate the free energy by the saddle-point method. In order to do so, we write the exponent:

$$A = A_G - \sum_r \log \left(\sum_{\alpha} \frac{1}{2} \varphi_\alpha^2(r) + e^{-\beta\epsilon} \sum_{\alpha < \beta} \varphi_\alpha(r) \cdot \varphi_\beta(r) \right). \tag{7}$$

The saddle-point equation $\partial A / \partial \varphi_\alpha(r) = 0$ reads

$$(\Delta_{rr}^\alpha)^{-1} \varphi_\alpha(r) = \frac{\varphi_\alpha(r) + e^{-\beta\epsilon} \sum_{\beta(\neq\alpha)} \varphi_\beta(r)}{\frac{1}{2} \sum_{\alpha} \varphi_\alpha^2(r) + e^{-\beta\epsilon} \sum_{\alpha < \beta} \varphi_\alpha(r) \cdot \varphi_\beta(r)}. \tag{8}$$

It is natural to look for a homogeneous and isotropic solution φ . This defines the isotropic mean-field (IMF). We break the $O(n)$ symmetry by choosing φ in a given direction, say 1.

We obtain

$$\varphi_1^2 = \frac{4}{d}. \quad (9)$$

At this mean-field level, the partition function and free energy per monomer read:

$$\mathcal{Z} \sim e^{-N+N \log q(\beta)} \quad (10a)$$

$$F_0 = -T \log \frac{q(\beta)}{e}. \quad (10b)$$

This is just the upper bound in (5). Note the similarity of (10a) with the equation $N_H = (q/e)^N$ of [13], counting the number of Hamiltonian paths on a lattice with coordination number q . We see that when $T \rightarrow \infty$ ($\beta\epsilon = 0$), we recover $q = 2D$, whereas, when $T \rightarrow 0$ ($\beta\epsilon = \infty$), $q = 2$, and the paths are fully stretched. There is a temperature T_F at which $q(\beta) = e$, and the free energy vanishes (in three dimensions, $T_F = 0.58\epsilon$). Below this temperature, the free energy becomes positive (with a maximum at $T_S = 0.31\epsilon$, where the entropy vanishes), in obvious violation of the bounds given in (5). Thus, it is clear that the IMF cannot be valid below T_F . These results are quite similar to the 'old' Flory theory [2], where $q(\beta)$ was replaced by $q(\beta) - 1$. Our results, however, give a much lower free energy.

The computation of the quadratic corrections to the saddle-point is easily done, by expanding the action (4) around φ_1 . There is one longitudinal mode and $(n-1)$ transverse modes associated with the breaking of the $O(n)$ symmetry.

The free energy per site reads

$$F_1 = -T \left[\log \frac{q(\beta)}{e} + \frac{1}{2L^d} \sum_{k \in \text{BZ}} \log \left(\frac{1 + A_T \sum_{\alpha=1}^d (1/u_{\alpha})}{1 + A_L \sum_{\alpha=1}^d (1/u_{\alpha})} \right) \right] \quad (11a)$$

where BZ denotes the first Brillouin zone: $k_{\alpha} = 2l\pi/L$, $l = 0, \dots, L-1$, and

$$u_{\alpha} = \frac{1}{2 \cos k_{\alpha}} - \frac{1}{q(\beta)} (1 - e^{-\beta\epsilon}) \quad (11b)$$

and

$$A_L = \frac{1}{d} - \frac{1}{q(\beta)} e^{-\beta\epsilon} \quad (11c)$$

$$A_T = -\frac{1}{q(\beta)} e^{-\beta\epsilon}.$$

We have computed the free energy F_1 as a function of the temperature in dimension $d = 3$. It turns out that f_1 is significantly larger than F_0 and since the latter was an upper bound, it indicates that the validity of the IMF is questionable.

If we remain at the IMF level, the result of the calculation is that there is a first-order transition between a high-temperature liquid-like phase ($T > T_F$) and a low-temperature frozen phase ($T < T_F$). This frozen phase does not come out as a solution of the saddle-point equation (8), but is dictated by the fact that the free energy of the model is necessarily negative. Physically, at zero temperature, the chain is fully stretched

(making its turns on the surface of the lattice); this one-dimensional character, which persists at low temperature [5, 6], cannot be treated adequately by mean-field, as is well known.

In order to cure the above-mentioned difficulty, we perform an anisotropic mean-field (AMF). We choose a direction 1, which we treat exactly, and we make a mean-field approximation on the remaining $(d-1)$ directions. Assuming a homogeneous and isotropic field φ in the $(d-1)$ directions, the partition function reads

$$Z_{AMF} = \lim_{n \rightarrow 0} \frac{1}{n} \int \prod_r d\varphi_1(r) \exp \left[-A_1 - \frac{N}{4} (d-1) \varphi^2 \right] \times \prod_r \left[\frac{1}{2} \varphi_1^2(r) + B\varphi \cdot \varphi_1(r) + C\varphi^2 \right] \tag{12a}$$

where

$$A_1 = \frac{1}{2} \sum_{r,r'} \varphi_1(r) (\Delta_{rr'}^1)^{-1} \varphi_1(r') \tag{12b}$$

$$B = (d-1) e^{-\beta\epsilon} \tag{12c}$$

$$C = \left(\frac{d-1}{2} \right) (1 + (d-2) e^{-\beta\epsilon}). \tag{12d}$$

We rearrange the product over r in (12a) as

$$\prod_r \left[\frac{1}{2} (\varphi_1(r) + B\varphi)^2 + \left(C - \frac{B^2}{2} \right) \varphi^2 \right]. \tag{13a}$$

Introducing n -vector spins S_r , with normalizations $S_r^2 = n$, $n \rightarrow 0$, together with the identity [15]:

$$\int d\mu(S) e^{H \cdot S} = 1 + \frac{H^2}{2} \tag{13b}$$

where $d\mu(S)$ is the normalized measure on the $O(n)$ sphere of radius \sqrt{n} , equation (12a) can be rewritten as:

$$Z_{AMF} = \exp \left[-\frac{N}{4} (d-1) \varphi^2 \right] D^{2N} \int \prod_r d\mu(S_r) \exp \left(\frac{1}{D^2} \sum_r S_r \cdot S_{r+e_1} + \frac{B}{D} \sum_r \varphi \cdot S_r \right) \tag{14a}$$

where

$$D^2 = \left(C - \frac{B^2}{2} \right) \varphi^2 \tag{14b}$$

and e_1 is the unit vector in direction 1.

The last integral in (14a) is a one-dimensional $O(n)$ model, with $n \rightarrow 0$, in a field. It can be easily computed by diagonalizing its transfer matrix. The two eigenvalues are given by

$$\lambda_{\pm} = \frac{1}{2} \left[1 + \frac{1}{D^2} + \frac{B^2 \varphi^2}{2D^2} \pm \sqrt{\left(1 + \frac{1}{D^2} + \frac{B^2 \varphi^2}{2D^2} \right)^2 - \frac{4}{D^2} \left(1 - \frac{B^2}{2D^2} \varphi^2 \right)} \right]. \tag{15}$$

The variational free energy per monomer reads:

$$F_{AMF} = T \left[\left(\frac{d-1}{4} \right) \varphi^2 - \log \left(\frac{1}{2} \left(1 + C\varphi^2 + \sqrt{(1 + C\varphi^2)^2 - 4(C - B^2)\varphi^2} \right) \right) \right]. \tag{16}$$

Minimizing F_{AMF} with respect to φ , we get the following results:

(i) There is a first-order transition at a temperature $T_C = T_{AMF}$. In $d=3$, $T_{AMF} = 0.68\epsilon$, slightly larger than T_F .

(ii) At low temperature $\varphi = 0$, and the polymer is fully stretched (crystal). At this mean-field order, the low-temperature phase is again inactive (full frozen), but it provides a sensible starting point for a systematic expansion.

(iii) At high temperature, $\varphi = 0$, and the free energy is very close to the IMF. It is a liquid-like phase, where the turns are mobile and entropically favoured. There appears a special point T_D , called a disorder point [10] of the second kind, at which the second eigenvalue λ_- vanishes, that is:

$$C = B^2. \quad (17)$$

In three dimensions, we find $T_D = 2.24\epsilon$. At this disorder point, the correlation length in direction 1 vanishes and thus the one-dimensional character of the paths disappear. There is an exact balance between the energy loss due to making turns, and the associated entropy gain.

Thus, for $T > T_D$, the liquid phase has isotropic short-range order, whereas for $T < T_D$, one-dimensional short-range order builds up announcing the low-temperature anisotropic ordered phase.

In figure 2, we plot the free energies of the IMF and AMF, and the lower bound of Gujrati and Goldstein [6]. At the transition point, $T_{AMF} = 0.68\epsilon$, the free energy of Gujrati and Goldstein is $\sim -10^{-6}\epsilon$.

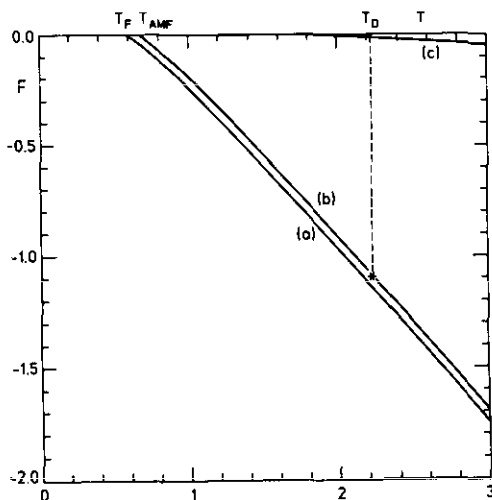


Figure 2. Free energy per monomer as a function of temperature. (a) Isotropic mean-field (IMF). (b) Anisotropic mean-field (AMF). T_D is the disorder point. (c) The upper bound of Gujrati and Golstein.

The fluctuations around the AMF can, in principle, be calculated. In the low-temperature phase, this calculation amounts to expanding around $\varphi = 0$; therefore, it is just a usual low-temperature expansion. The lowest-order excitation† is shown in

† Note that equation (18) holds only if one expands around the ground state where all the bulk monomers are parallel.

figure 1 and yields:

$$F = -(d-1)T e^{-6\epsilon/T}. \quad (18)$$

It is thus negative, but again very small, since at T_{AMF} , $F = -1.76 \times 10^{-4}\epsilon$. In the low-temperature phase, the average number of aligned monomers between two corners (related to the inverse of the internal energy) is exponentially large: equation (18) indeed yields $l \approx e^{6\epsilon/T}/6(d-1)$, so that the low-temperature phase can be viewed as frozen (almost fully stretched). For $d=3$, we find $l \approx 566$ at T_{AMF} .

We have not been able to perform the full calculation of fluctuations in the high-temperature phase, but the smallness of the fluctuations in the low-temperature phase strongly suggests that the AMF captures the correct physics. Finally, figure 2 shows that IMF and AMF are very close.

In conclusion, we have presented a new mean-field theory for the Flory model of polymer melting. We find a first-order transition between an almost stretched phase at low temperature and a liquid phase at high temperature. The low-temperature phase is characterized by a weak temperature dependence, and the overall phase diagram is qualitatively consistent with the Flory picture [2]. We find also a disorder point T_D in the liquid phase, which is the boundary between two types of short-range correlations (isotropic and one-dimensional). This is similar to the '2 T_C ' point in the F -model [8, 16]. In simple spins systems, it has been shown [17] that disorder points lead to a slowing down of the dynamics. In a dense polymeric system such as the one considered here, the dynamical implications are likely to be much more severe. It is thus tempting in these (and perhaps other) systems to relate the disorder point to the glass transition, in contrast to the Gibbs and Di Marzio [18] theory of the glass transition.

We thank H Saleur for drawing our attention to the polymer melting literature.

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