

# Statistical thermodynamics of polymer crystallization

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A survey was made on the recent development of the mean-field lattice theory of polymer solutions to predict the properties of equilibrium melting points of bulk polymers. The interaction parameters were identified for several real polymers.

**Keywords** polymer, statistical thermodynamics, crystallization, melting points

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## 1 Introduction

Polymer melting and crystallization have been regarded as one of the most important macroscopic properties in engineering polymeric materials such as plastic molding and fiber spinning. Statistical thermodynamics serves as a bridge to cross over the gap between molecular parameters and macroscopic properties. However, its success rests very much upon proper modeling of molecular parameters. In this review article, we make an overview on our recent efforts devoted to the establishment of proper molecular parameters for statistical thermodynamics of polymer crystallization and to its applications in the prediction of melting-point properties. Some efforts on specifying the energy parameters of several real polymers were introduced in the end.

## 2 Establishment of molecular parameters

Polymer chains are locally anisotropic connection of monomers by structural definition. Such an anisotropic feature endows locally anisotropic interactions to the packing of polymer chains. The anisotropic interactions have been regarded as the molecular driving forces for isotropic-nematic ordering of liquid-crystal mesogenic particles, including the Maier-Saupe anisotropic attractions for thermotropic phase transitions in the bulk phase [1,2], and the Onsager anisotropic repulsions for lyotropic phase transitions in solutions [3]. Flory cited Onsager's idea to regard the anisotropic repulsion induced by chain rigidity as the molecular driving forces for spontaneous ordering of polymers at low temperatures.

However, such a repulsion has not actually been considered in his lattice statistical theory of semiflexible polymer solutions [4]. On the other hand, concerning the fact that all the crystalline polymers are always packing their backbone chains in parallel, Hu introduced the Maier-Saupe-type anisotropic attractions for spontaneous crystallization of polymers [5]. In the lattice model, these attractions are represented by the parallel packing interactions of polymer bonds [5]. The corresponding lattice statistical theory of semiflexible polymer solutions was thus developed on the basis of Flory's lattice theory by employing a mean-field treatment of parallel attractions of lattice polymer bonds [6,7]. In the next section, we will make a more detailed introduction about this approach.

## 3 Lattice statistical theory of polymer solutions

In an NVT system in which particle number, volume, and temperature are all constant, the main goal of statistical physics is to derive the partition function for all the microstates. In practice, due to the tremendous amount of microstates, one can not exhaustively count all the possible microstates but must obtain necessarily representative distribution of microstates in the energy space. As has been well known, such a distribution is a summation of Boltzmann's distributions with an exponential dependence of energy levels and a prefactor of combinatorial amount in each energy level. What we have usually done is to make a mean-field assumption to separately estimate the total energy of microstates and the total combinatorial amount of microstates. According to the Boltzmann relation, they correspond to the energy and entropy

in the constitution of free energy, respectively. Their multiplicity gives the expected partition function.

Let us start from the estimation of the combinatorial entropy of polymer solutions. We take the fully ordered and phase-separated state as the ground state. Assume that we have  $n_1$  solvent sites and  $n_2$  polymer chains, each chain occupies consecutive  $r$  monomer sites, in a regular lattice (the coordination number is  $q$ ), hence the total volume of the lattice is  $n = n_1 + rn_2$ . The partition function of the combinational entropy in the homogeneous phase of polymer solutions is given by:

$$Z_{\text{comb}} \approx \left(\frac{n}{n_1}\right)^{n_1} \left(\frac{n}{n_2}\right)^{n_2} \left[\frac{q(q-1)^{r-2}}{2e^{r-1}}\right]^{n_2}. \quad (1)$$

This result is actually derived under the classical Flory-Huggins lattice theory for flexible polymer solutions. For semiflexible polymers, Flory introduced an energy parameter  $E_c$  for the potential energy difference between linear (one direction) and nonlinear ( $q-2$  directions) connections of the consecutively next bond along the lattice chain [4]. There exists the conformational partition function for each bond connection, as given by:

$$z_c \equiv 1 + (q-2)\exp\left(-\frac{E_c}{kT}\right), \quad (2)$$

in which  $k$  is Boltzmann's constant, and  $T$  is the temperature. Replacing the possible amount of bond connections  $q-1$  in Eq. (1) with  $z_c$ , we obtain the partition function of the combinatorial entropy as:

$$Z_{\text{comb}} \approx \left(\frac{n}{n_1}\right)^{n_1} \left(\frac{n}{n_2}\right)^{n_2} \left(\frac{qz_c^{r-2}}{2e^{r-1}}\right)^{n_2}. \quad (3)$$

Next, we estimate the mixing energy contributed by the mixing pairs of solvent and monomers in the lattice model. Following the quasi-chemical approximation in the classical Flory-Huggins lattice theory, the net energy of each mixing pair is defined as:

$$B \equiv E_{12} - \frac{E_{11} + E_{22}}{2}, \quad (4)$$

where  $E$  represents the pair attractions, and the subscriptions '1' and '2' represent the solvent and monomers, respectively. Under the protocol of the mean-field assumption, the partition function contributed by the total mixing energy is thus given by:

$$z_m \equiv \exp\left[-(q-2) \cdot \frac{n_1}{n} \cdot \frac{B}{kT}\right]. \quad (5)$$

Similarly, the partition function contributed by the total packing energy of those nonparallel bonds is given by [6]:

$$z_p \equiv \exp\left\{-\frac{q-2}{2} \cdot \left[1 - \frac{2(r-1)n_2}{qn}\right] \cdot \frac{E_p}{kT}\right\}. \quad (6)$$

The total partition function of polymer solutions is thus the multiplicity of the three part contributions shown above, as given by:

$$Z = \left(\frac{n}{n_1}\right)^{n_1} \left(\frac{n}{n_2}\right)^{n_2} \left(\frac{q}{2}\right)^{n_2} z_c^{(r-2)n_2} e^{-(r-1)n_2} z_p^{(r-1)n_2} z_m^{rn_2}. \quad (7)$$

With this partition function, one can calculate the equilibrium melting point of bulk polymers as well as the phase diagrams of polymer solutions and blends, as we will proceed in the next section.

## 4 Properties of melting points

For bulk long-chain polymers,  $r \gg 0$ ,  $n_1 = 0$ , and  $n = r \cdot n_2$ . The partition function in this case can be simplified as:

$$Z = \left(\frac{qr}{2}\right)^{n_2} z_c^{(r-2)n_2} e^{-(r-1)n_2} z_p^{(r-1)n_2}. \quad (8)$$

Since the free energy  $F = -kT \ln Z$  equals to zero, one can obtain the equilibrium melting point from:

$$1 + (q-2)\exp\left(-\frac{E_c}{kT_m^0}\right) = \exp\left[1 + \frac{(q-2)^2}{2q} \cdot \frac{E_p}{kT_m^0}\right], \quad (9)$$

where  $T_m^0$  is the melting point. If polymers are quite flexible, i. e.,  $E_c < kT_m^0$ , we can omit the first term on the left-hand side and further simplify the above equation into:

$$T_m^0 \approx \frac{E_c + \frac{(q-2)^2}{2q} E_p}{k[\ln(q-2) - 1]}. \quad (10)$$

Now, Eq. (10) becomes more intuitive for the relationship between the molecular energy parameters and the melting point. Larger  $E_c$  implies higher rigidity of polymers and gives higher melting point. On the other hand, larger  $E_p$  implies stronger interchain interactions or smaller side groups favoring compact packing, giving higher melting point as well. Such relationships can actually be found from our experience on the comparisons of melting points among real polymers [8].

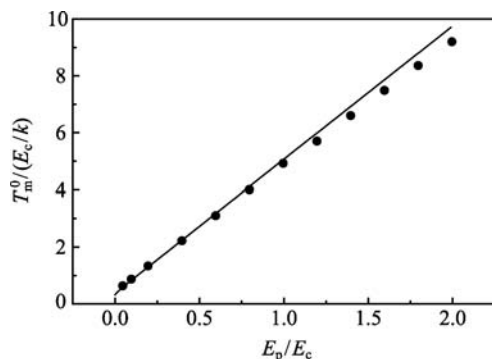
More precisely, the melting point of bulk polymers with limited chain lengths at  $r$  can be calculated by inserting the partition function of Eq. (7) into the equation since the free energy  $F = -kT \ln Z$  equals to zero, as given by [7]:

$$(1-r) \frac{n_2 r}{n} + \ln \frac{qn}{2n_2} + (r-2) \ln \left[1 + (q-2) \exp\left(-\frac{E_c}{kT_m^0}\right)\right]$$

$$= \frac{(r-1)(q-2)}{2} \left[ 1 - \frac{2(r-1)n_2(n+n_1)}{qn^2} \right] \frac{E_p}{kT_m^0} + \frac{rn_1^2(q-2)B}{n^2 kT_m^0}. \quad (11)$$

In practice, we can use  $E_c/k$  as the unit of temperature and adjust the reduced energy parameters, such as  $E_p/E_c$  and  $B/E_c$ . By solving Eq. (11) through iteration, one can obtain the theoretical equilibrium melting point for any preset molecular parameters.

Figure 1 compares the theoretical predictions of Eq. (11) with the parallel results of molecular simulations of bulk polymers [7]. One can see a good consistence between theory and simulations, verifying the validity of the mean-field assumption in the theory. Both the simulation data and the theoretical curve appear roughly linear dependence, as predicted by Eq. (10). Figure 1 again demonstrates that the larger the parallel packing interactions, the higher the melting points.



**Figure 1** The curve of melting temperatures of polymers ( $T_m^0/(E_c/k)$ ) with variable  $E_p/E_c$  values. The line is calculated from Eq. (11), and the spheres are simulation results obtained from the onset of crystallization on the cooling curves of disorder parameters, in a short-chain ( $r = 32$ ) system (occupation density is 0.9375 in a 32-sized cubic box) with a template substrate [7].

Chain length is another structural factor influencing the melting point. Flory suggested a semi-empirical theory for the chain-length dependence of melting points, which was shown in consistency with experimental data [9]. They assumed that polymer melting proceeds in virtually two steps: the first step is the melting of infinite chain length and the second step brings an additional free energy change by cutting the chain into segments of definite lengths. At the equilibrium melting point, one obtains:

$$\Delta f_m = r\Delta f_u + \Delta f_c - kT_m^0 \ln r = 0. \quad (12)$$

The free energy change  $\Delta f_u$  on the melting of each repeating

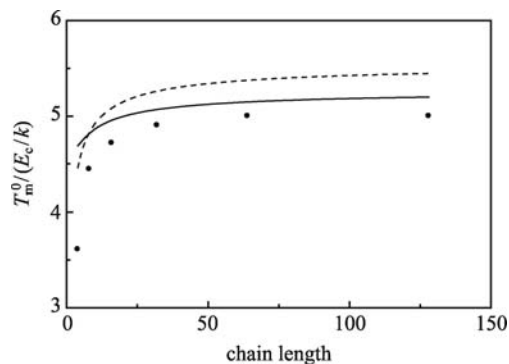
unit can be roughly obtained from Eq. (10) based on the thermodynamic equilibrium condition  $T_m^0 = \Delta h/\Delta s$ , as given by:

$$\Delta f_u = r\Delta h_u - T_m^0 \Delta s_u = E_c + \frac{(q-2)^2}{2q} E_p - kT_m^0 [\ln(q-2) - 1]. \quad (13)$$

The additional free energy change on cutting at chain ends can be calculated from Eq. (11) by setting  $r = 2$ , as given by:

$$\Delta f_c = \frac{(q-2)(q-1)}{2q} E_p - kT_m^0 (\ln q - 1) - 2\Delta f_u. \quad (14)$$

Taking Eqs. (13) and (14) into Eq. (12), one can solve the Flory melting points as shown in Figure 2. In this figure, we compared the theoretical predictions of melting points calculated from Eq. (11) for variable chain lengths with Flory predictions and the simulation results of parallel sample systems. The results show a quite consistency between each other. At the shorter end of polymer chains, the melting points are of strong dependence on chain lengths; while at the longer end, they become insensitive to chain lengths.



**Figure 2** Melting temperatures of polymers ( $T_m^0/(E_c/k)$ ) with variable chain lengths. The solid line is calculated from Eq. (11), the dashed line is calculated from the Flory analysis (Eq. (12)), and the spheres are the simulation results. In simulations, the occupation density is 0.9375, and the linear size of the cubic box is set to 32 for short chains and 64 for long chains [7].

Dilution with small molecules like solvent and plasticizers brings a depression of melting points to polymers. Flory has derived a semi-empirical equation to predict the melting-point depression of polymer solutions [9], as given by:

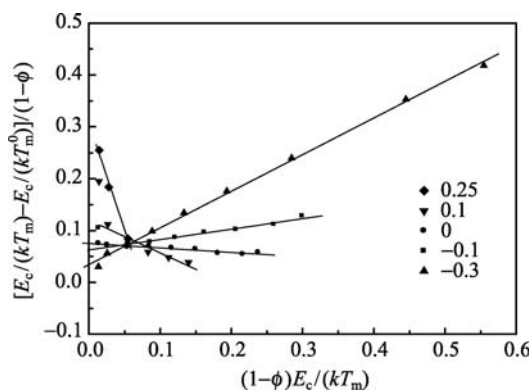
$$\frac{1}{T_m} - \frac{1}{T_m^0} = \frac{k}{\Delta h_u} [1 - \phi - \chi(1 - \phi)^2] \quad (15)$$

Here,  $\phi$  is the volume fraction of polymers in solutions, and  $\chi$  is the mixing interaction parameter reflecting  $B$ . By reformulating the melting points of polymers obtained from

**Table 1** Thermal data and estimation of interaction parameters of several polymers [10]

| polymer | $T_m^0/\text{K}$ | $\Delta H_m/(\text{J}\cdot\text{mol}^{-1})$ | bonds | $q_{\text{eff}}$ | $E_c/(\text{J}\cdot\text{mol}^{-1})$ | $E_p/(\text{J}\cdot\text{mol}^{-1})$ | $E_p/E_c$ |
|---------|------------------|---|-------|------------------|--------------------------------------|--------------------------------------|-----------|
| PE      | 419              | 4016.64                                     | 1     | 10.6             | 2092                                 | 549.90                               | 0.263     |
| PTFE    | 605              | 4100.82                                     | 1     | 8.1              | 2928.8                               | 509.57                               | 0.174     |
| iPP     | 459              | 8786.4                                      | 2     | 29.2             | 6276                                 | 197.67                               | 0.031     |
| POM     | 457              | 9800  | 2     | 37.8             | 6276                                 | 207.29                               | 0.033     |
| PEO     | 342              | 8660  | 3     | 59.1             | 418.4                                | 298.61                               | 0.714     |

the simulations of polymer solutions, we did observe the linear dependence predicted in Eq. (15), as demonstrated in Figure 3.



**Figure 3** Melting points of polymers in relation with polymer concentrations. The bulk equilibrium melting temperature  $E_c/(k \cdot T_m^0)$  is chosen to be approximately 0.2. The lines are the results of linear regression, and the symbols are for the variable values of  $B/E_c$  [6].

## 5 Specification of molecular parameters

By fitting Eq. (10) with the formula of  $T_m^0 = \Delta H_m/\Delta S_m$ , we obtain the practically useful expression as:

$$T_m^0 \approx \frac{\Delta H_m}{R[\ln(q-2) - 1]} \quad (16)$$

Here,  $R$  is the molar gas constant. Therefore, with the experimental data for  $T_m^0$  and  $\Delta H_m$ , one can obtain  $q$ . The value of  $q$  actually represents the effective coordination number of each repeating unit when it is mapped into the lattice site. Furthermore, if we have the data of  $E_c$ , we can obtain  $E_p$  according to:

$$\Delta H_m = E_c + \frac{(q-2)^2}{2q} E_p \quad (17)$$

The results of several common polymers are summarized in

Table 1 [10]. One can see that the longer repeating units provide larger  $q$  values. Isotactic polypropylene (iPP) has relatively small  $E_p/E_c$  values, implying the weak molecular packing energy which may make polymorphism occur upon crystallization. More details can be found in Ref. [10].

## 6 Summary

We made an overview on the statistical thermodynamics of polymer crystallization. The energy parameter for parallel packing of crystalline polymers ( $E_p$ ) is modeled as the key driving force of polymer crystallization. Many molecular simulations of polymer crystallization root on this assumption. A mean-field treatment of this interaction yields reasonable predictions of melting-point properties as proven by the parallel results of molecular simulations. Several common polymers were identified on their  $E_p$  parameters. More other polymers are still demanding big efforts for the identification of their  $E_p$  parameters.

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