On the kinetics of polymer crystallization: a possible mechanism

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Abstract

In this study, we propose the dispersive ("long-tail") kinetics concept as a possible candidate for elucidating qualitatively some experimentally noticed departures from the constancy in a polymer crystal growth rate against time behavior. It turns out to be a consequence of some more detailed consideration of the polymer (colloid) mass-dependent diffusion coefficient, which is consistent with a microscopic picture of the entire crystallization phenomenon, that is basically a nucleation-and-growth process. The phenomenon under consideration appears to be solution controlled, with a dominant role of solute or solute-solvent interactions. The random adsorption of macromolecules cannot drastically change this picture.

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1 Introduction

A development of the modern science of crystal growth goes nowadays towards getting possibly deep insight into elementary mechanism(s) of this phenomenon. The same can also be noticed for a polymer crystal growth (or, for related processes, e.g. those, containing viruses, or even constituting inorganic hydrates), where the crystals grow from (aqueous) solution, mostly if the solution is brought into supersaturation. There
are a few standard and well established [1], and some others, perhaps more specific, but most frequently equally powerful [2] theories, that try to embark on this difficult task termed the mechanism of the kinetics of polymer crystallization. Many crystallization experiments have been performed recently [3] using, e.g. such proteins, like lysozyme, canavalin, or viruses e.g., cubic satellite tobacco mosaic virus. Also, one may find in the literature a good number of experiments, in which inorganic (oligomeric) crystalline hydrates, e.g. asparagine and rhamnose monohydrates or calcium oxalate trihydrates, have been obtained [4-7].

In this work, the kinetics of the crystallization from a (supersaturated) solution for systems mentioned are proposed for consideration. The process that we are going to study appears to be a complex phenomenon the mechanism of which is basically a nucleation-and-growth phase transition (typically, thermally activated) [1-4, 8]. In reality, it proceeds on a good number of mobile nuclei and is recognized as being realized via some random accretion (also, deposition) of subunits (monomers or clusters) at growing crystallization centers. The subunits, in turn, are observed to emerge in a random manner, i.e. by random attachment and/or detachment of smaller subunits (in particular, monomers). After the clusters are being formed their centers of inertia follow a Random Walk, till the accretion process is successfully completed. In this way, under a given set of known parametric physicochemical conditions, like temperature, pH, solute concentration, pressure, presence of impurities, etc. [1-3], larger and larger (poly)crystals are expected to emerge. Applying the mass conservation law for the growing crystal, one is capable of determining how fast does the object evolve into its nutrient phase. Because the mass feeding proceeds via sticking of units that are sometimes bigger than the monomers, it was suggested [9, 10], that the attachment/detachment, i.e. chemical reaction rate, or equivalently (for a three-dimensional or 3d-case), the diffusion coefficients depend upon time. It is possible to state, because such time dependences have been obtained theoretically (cf. [10] for details), and they show those coefficients to be inverse powerly time-dependent, which resembles very much the principal assumption of the dispersive (or fractal-like) kinetics concept [11]. A certain privilege is that the model offered contains, inspite the set of parametric conditions that have to be known (see above), exclusively two parameters to be estimated: an averaged fractal dimension of diffusing clusters as well as the polymer-polymer interaction parameter that we will call a Flory-Huggins-like interaction parameter, belonging to [0, 1]. The value of this parameter is also changed if a type (or, characteristics) of solvent is changed. If this parameter is set to be one, the interaction of two polymer chains, or assemblies of them, succeeds, with probability equal to one; if it is less than one, the probability of success is certainly less than one [12]. (The former corresponds to the fast diffusion-controlled regime of the process, whereas the latter can be related to the slow chemical reaction regime [9, 10, 13].)

## 2 Description of the process

It is known that if one wishes to determine how fast the (poly)crystals can grow, one
has typically to make use of a continuity equation. This continuity equation is simply the mass conservation law, which tells us that the mass, feeding the growing crystal, comes mostly from the Brownian field in which the object(s) is (are) immersed [1, 8].

Because in this paper, we would like to confine ourselves to sketch the main tendencies rather, paying minor attention to some very important details, that can be found elsewhere [1, 2, 8], let us use the continuity equation in a simplified form [14, 8, 1], namely

$$\frac{dM}{dt} = \overline{D} \left( \frac{dC}{dr} \right)_{\text{surf}} S,$$  \hspace{1cm} (1)

where the left-hand side of eq. (1) represents the rate of deposition of polymer mass at the crystal surface, \( \overline{D} \) stands for the diffusion coefficient averaged over all possible values [1, 10, 4, 16, 6], \( S \) is the crystal surface area, and finally, \( (dC/dr)_{\text{surf}} \) is the concentration gradient (evaluated for a difference between the bulk and interface concentrations of solute with respect to the effective width of the diffusive field) taken at the corresponding interface [14].

In this study, we wish to work out the crystallization process realized in a three-dimensional space, i.e. for \( d = 3 \). Without loosing generality, let us assume that homogeneous biopolymeric crystals of density \( \rho \) evolve in course of time \( t \), and that, for simplicity, they are of spherical form; here, the radius of the sphere is designated by \( R \equiv R(t) \). Utilizing well-known geometrical relations, like \( M = (4\pi/3)\rho R^3 \) and \( S = 4\pi R^2 \), and putting into eq. (1), we get immediately (the radial direction is now \( r = R \))

$$\frac{dR}{dt} = \frac{\overline{D}}{\rho} \left( \frac{dC}{dR} \right)_{\text{surf}},$$  \hspace{1cm} (2)

which is possible to sustain as a crude, yet still reasonable approximation of the growth rate, if one assumes that the molar volumes of solute and solvent are balanced in the crystalline and bulk phases [14]. Moreover, assuming that \( \overline{D}/\rho \) as well as \( (dC/dR)_{\text{surf}} \) are independent of time \( t \), that means, a typically met case [1], utilizing (2), one arrives easily at the asymptotic dependence, like \( R \propto t \). Note, however, that for pure diffusion-controlled crystallization processes a relationship, like \( (dC/dR)_{\text{surf}} \propto 1/R \) can be appropriate, so that instead of \( R \propto t \), one must get \( R \propto t^{1/2} \) [1, 8], but this is rather a case characteristic of systems composed of small (light) solute molecules [1], not of heavy macromolecules, for which some convective or even microgravitational effects may play a significant role [3, 2]. In other words, the polymer crystal growth rate, \( V_g \), defined as \( V_g = dR/dt \) is constant in course of time \( t \), at least, at this stage of the simple approximation recalled. It is true for a certain number of polymeric (spherulitic) crystals [4, 6, 8]. E.g., as reported by Kam et al. [14], and confirmed by others [2, 3, 4, 6], it seems to be also the case when the deposition of protein mass proceeds via monomers. For dimers and other \( k \)-mers, viz. clusters, a time dependence for \( \overline{D} \) has to be expected. It is logical since the adsorption of dimers and mers of higher order would need more time to be realized effectively. Note that this picture by no means contradicts a commonly accepted scenario of dislocation controlled protein crystal growth, drawn by Burton et al.. Scattering (light, neutron, X-ray) methods give, however, clear evidences that it
proceeds via direct incorporation of monomers into the crystal lattice; c.f. literature listed in [3]. The question to be posed here is: which time dependence is appropriate in this case?

To answer this question, let us recall that a strikingly similar kinetic behavior for, e.g., protein solutions and some colloidal or surfactants-containing systems (e.g., silica or polystyrene spheres of micrometer size in solutions, gold particles in a suspension [9, 17, 16, 10]) has been found on both the experimental [15, 9] as well as theoretical [10, 18] levels. In particular, it was found that the average number of resulting fractal clusters (or, microcrystallites [9]) is a decreasing function of time, being of the same scaling form for the two systems compared, and that generally speaking, the cluster-cluster aggregation process is going to be slowed down, no matter in which regime (diffusion, with a sticking probability, \(p_s\), equal to one, or chemical reaction, with \(0 < p_s < 1\)) one is attempting to investigate it [9]. The only exception is when \(p_s = 0\), but this case must be excluded because there is no cluster-cluster (e.g., monomer-monomer) aggregation. Equivalently, this can be the case of the monomer deposition, which has been solved by Kam et al. [14], and resulted in a constant growth rate \(V_0\).

Let us now consider the quantity \(\bar{D}\) that is crucial in our further investigations. As first found out by Kirkwood [12], and more recently followed by others [19], the diffusion coefficient in a polymer solution is given by

\[
\bar{D} \sim M^{-\nu},
\]

where \(M\) is the mass of the polymeric cluster and \(\nu\) stands for the characteristic exponent, which is, on the basis of some theoretical grounds [12, 19], set to be 3/5 (this is the scaling exponent for the so-called "real" polymeric chain, with excluded volume effect, due to polymer-solvent interaction). There exist, however, many rather small, but sometimes important departures from the value of 3/5 [12, 15, 9, 19], generally due to polymer-polymer as well as polymer-solvent interactions, noticed even in a regime of the diluted polymeric solutions [12]. (Since we have assumed that the polymer is immersed in a solvent with a positive excluded volume effect [12], the latter would be, however, taken as being of minor influence on our further study.)

In the era of modern computers it was realized [9, 17] that \(\nu \approx 1/d_f\), where \(d_f\) stands for the fractal dimension of a diffusing cluster [10]. It is rather a certain approximation, which neglects the very crucial interaction effects [12]. We are of the opinion, that the situation can be modelled properly when we are exactly in the diffusion limit of the cluster-cluster aggregation process, i.e. with \(p_s = 1\), which means, that each collision of two clusters results in producing a new and bigger one. If the success is uncertain, we are in the chemical reaction (more realistic) regime, with \(0 < p_s < 1\). Thus, like in [13], where some coagulation kinetics were described, we need an interaction parameter. Looking at a list of parameters accepted in polymer physics we see, in a natural way, a certain good candidate for the first choice. So, let us propose a Flory-Huggins-like interaction parameter, \(\kappa\), that is responsible for the polymer-polymer interactions in the system, which can result even in, e.g., making from a diluted solution a semi-diluted because of the entanglement effects, that apparently change the viscosity of the solution [12]; see also some theoretical arguments provided in [19]. (The spinodal decomposition, nonsteady
precipitant-impurities repartitioning, imperfect stirring, ion segregation, correlational as well as rheological effects may likely appear as well [9, 6, 13, 11].

In the light of what has been stated above, we wish to propose, instead of taking $\nu$ in relation (3) either about $3/5$ or as $1/d_f$ (see [10]), that we will choose

$$\nu = \frac{\kappa}{d_f},$$

where $\kappa \in (0, 1]$; it is a dimensionless parameter, being generally responsible for the solute-solvent interactions. It means, that we are, in principle, slightly out of the (idealistic) good-solvent regime, but we can still have a 'poor' solvent with a positive excluded volume effect, ensuring interactions among polymeric chains, however [12]. Typically, some estimation of the Flory-Huggins parameter yields $\kappa \in [0.4, 0.6]$, but a theoretical value of 0.76 for a diluted solution made of flexible chains dispersed in a (good) solvent, has also been picked up [12]. In our approach, which must be consistent with the previous studies [10], we take limit $\kappa = 1$, when the cluster-cluster aggregation process is purely diffusion-controlled. Otherwise, i.e. for $\kappa \in (0, 1)$, it is more or less chemical reaction limited. In this way, we introduce a mechanism of the anomalous diffusion of fractal clusters of dimension $d_f$, that do interact with one another with some interaction strength $\kappa$, and the mass of which typically increases with time $t$. (A more general case has been worked out in [10], where the mass of clusters increased on average with time, but, because of random attachment or detachment (dissolution) of particles or other clusters, due to Poissonian statistics or linear birth-and-death process rules, the system showed sometimes also a standard diffusional behavior [10, 16] since, no surprise, the net effect was that the mass was unchanged after such a realization of the process. In [10, 9] it has been shown that if diffusing particles aggregate randomly, then effectively the mass of the aggregate increases with time when the statistics of attachment events is Poissonian and, in consequence, diffusion is such as with the effective diffusion function given below by (6). This is, however, not true for other, say non-Poissonian, statistics.)

Thus, the most typical (for sure, confirmed also by a deterministic approach, cf. [16, 10]) result was [10, 9, 16] that a linear increase of the cluster's mass in course of time $t$ has to be taken into account, namely

$$M = M_0\left(1 + \frac{t}{t_c}\right),$$

at least, for sufficiently large times $t$ and when assumed that the attachment events may eventually prevail; here, $M_0$ is the initial mass of the growing cluster, performing a Random Walk, and $t_c$ stands for a characteristic time, which is the mean time between the subsequent attachments of molecules to the crystal, fully available from the Poissonian statistics. (Let us take, without losing generality, $t_c = 1$ because the reason for incorporating $t_c$ is mostly to ensure the correct units for mass $M$.) It enables to write down the diffusion coefficient as follows (see eqs. (3)-(5))

$$\bar{D} \sim [M_0(1 + t)]^{-1/D_f}.$$
where $D_f = 1/\nu \equiv d_f/\kappa$. This is now the interaction-influenced "fractal dimension", so that some restructuration of the clusters in the solution, due to polymeric interactions [12], may additionally be accomplished this way [9, 17]). Note that $D_f \in [1, \infty)$ (cf. [13] and eq. (4) therein, for a comparison possible when substituting that $\lambda$, describing a reactivity of two big clusters, by $1 - \kappa$, or even by $1 - \nu$, taken from eq. (4) written above).

It is possible to invent another argumentation, supporting that a scaling law, like that given by eq. (6), holds. One can rationalize it twofold. First, one may notice that eq. (3) (and, in consequence, eq. (6)) comes from the Stokes-Einstein (SE) formula

$$D = \frac{kT}{C\eta R_m},$$

where $R_m$ stands for the radius of the diffusing molecule or cluster (note that a scaling relation $R_m \sim M^\alpha$ should hold for the case studied!), $k$ is the Boltzmann constant, $T$ is the absolute temperature, and $\eta$ represents the shear viscosity of the solution. In turn, $C$ stands for a constant, depending on the geometrical characteristics of diffusing molecules. In several polymeric solutions, e.g. in serum albumin-water systems, mostly due to an increasing $H$-bonds production in the vicinity of the surface of diffusing object, the SE-formula is clearly violated [15, 19], which results in substitution (in SE-formula written above) of $R_m$ by the effective hydrodynamic radius $R_h$ [16]. It mostly implies that the fluid near the surface of the diffusing object is more viscous than the bulk, which provides an increase of $R_h$ when compared with $R_m$. If, in turn, $R_h$ scales powerly with time $t$ [12], like $R_h \sim t^\nu$ (asymptotically), one can easily recover, utilizing again SE-formula, relation (6). Second, one can make use of some apparent analogy between a primary crystallization in amorphous alloys (e.g., $\alpha - Fe(Si)DO_3$), which is a kind of diffusion-controlled grain growth, driven by the Avrami-Kolmogorov (AK) phase change kinetics [20], and the protein crystallization from a solution containing impurities, sometimes also rationalized in terms of the AK-concept [2,3]. It concerns with a competition between available excess solute, which leads to an overlapping effect for the diffusion fields of neighboring grains (microcrystallites). Under such circumstances, $D$ is not a constant [20], but it is inversely proportional to the fraction of transformed phase, $Y$, which, as a consequence, gives a decrease of $D$ with time $t$. Since $Y = 1 - X$, where $X$ stands for the fraction of untransformed phase, which, in general, has proved to decrease with $t$ as $X \sim \exp[-(t/\tau)^\mu]$, with $\mu$ being another exponent (belonging to $[0,1]$), possibly very much related to $\nu$, and $\tau$ representing the characteristic (relaxation) time of the system, expanding $\exp$ up to quadratic terms (or, using the linear approximation, which implies that $\tau \gg 1$), one may typically get $Y \sim t^{-\mu}$, or equivalently, that $D$ may powerly decrease with time, even for a very mature stage of the growing process (for a rationale, cf. [21], and refs. therein).

Additional arguments, on the possible manifestation of the dispersive kinetics (crudely speaking, the kinetics with $D \sim t^{-\mu}$, asymptotically) [11] in the system studied, can be:

(i) existence of different solubilities and swelling conditions [5] for the crystalline and non-crystalline states;

(ii) influence of impurities (e.g., NaCl) as well as structural (e.g., due to imperfect stirring
of the solution) and depletion effects on the kinetic conditions [6];
(iii) anomalous strain-stress response within the system as a whole [4, 6].

3 Asymptotic kinetic relations characterizing the phenomenon

To determine the asymptotic forms of the diffusion coefficient(s) (just for brevity;
a much more elaborated formulae one can find elsewhere [10]), one has to make use
of the recepies given, e.g. in [10] or seminal stochastics textbooks, which results in
formulating the problem in terms of a standard diffusion equation for the probability
$p(x, t)$ of finding the center of mass of a fractal cluster (with the fractal dimension $D_f$) at
a space position $x$ and at time $t$, but with the diffusion function of (6). Then, we have to
solve $p_t(x, t) = \bar{D}\Delta p(x, t)$, where $p_t$ and $\Delta$ (Laplacian) have their usual meanings [10, 16],
evaluate the mean squared displacement, $< x^2(t) >$, as the second moment of the process,
namely $< x^2(t) > = \int_0^\infty x^2 p(x, t) dx$ (by the way, the process appears to be non-Gaussian
as well as non-Markovian [10]), and differentiate it with respect to $t$. It provides
the effective macroscopic diffusion coefficient $D_{eff} = d< x^2(t) >/dt$ (very large compared to
$\bar{D}$, but since now a readily averaged and, no doubts, time-dependent quantity, taken as
a formal substitute of $\bar{D}$ in our model ) to scale as

$$D_{eff} \sim t^{-1/D_f}, \quad \text{for} \quad D_f > 1,$$

and

$$D_{eff} \sim t^{-1}, \quad \text{for} \quad D_f = 1. \quad (7)$$

The latter (eq. (8)) represents the effective anomalous diffusion coefficient for aligned
(rod-like) polymers or polymeric assemblies ($d_f = 1$), when the cluster-cluster aggregation
is under pure diffusional control ($\kappa = 1$; the interaction is the strongest). It may result
in the most effective crystallization of polymers, because (replace $\bar{D}$ by $D_{eff}$ and solve
eq. (2), in the "long" times limit, for clarity)

$$R \sim \ln(t), \quad (9)$$

which means, that $V_p$, given as $dR/dt$ (see above), is going to decrease quite rapidly
with $t$ as $1/t$, and the process goes down.

In this same way, but making use of eq. (7), one gets at once, but for $D_f > 1$, or
equivalently, for the case of $d_f > \kappa$ (notice that $d_f \in [1, 3]$)

$$R \sim t^{1-\frac{D_f}{2}}, \quad (10)$$
i.e. a power law is recovered for the behavior of crystal radius against time. In this case, $V_g$ is going to decrease with $t$ as $1/t^{1/D_f}$, that is apparently slower than in the preceding case. One must notice that $V_g$ is going to change in time in the same way as $D_{eff}$ does. We see from [14, 2] that eqs. (9) and (10) confirm qualitatively a picture of the polymer as well as oligomeric crystallization drawn. Moreover, let us realize that now, inspite the limiting case $D_f^{-} = \infty$ (or, $\kappa^{-} > 0$, i.e. a very reactive case !), there is no constant growth rate $V_g$ as was mentioned in [14]. It is so, indeed, because presence of clusters bigger than monomers, and possibly, all the external field effects mentioned, can change, even drastically, the situation that we have described. The exponent specified as

$$1 - \frac{1}{D_f} \equiv 1 - \nu \in [0, 1]$$

can take, in some reaction limits (for $D_f^{-} > 1$), on very small values, which does explain also very long times of the effective crystallization of some biopolymers, like lysozyme, ADP [2, 3, 4, 14, 6], or colloids [9]. Moreover, notice that such a critical exponent is very characteristic of many growing systems, where the process is realized in a competitive manner, like dynamic epidemics, or advancement of an interface, which borders a condensed phase consisting of two species competing with each other (a binary "alloy"), i.e. a phase separation effect [22].

4 Conclusion and perspective

In conclusion, let us state that in the present study, some approach to the kinetics of polymer crystallization, being solution controlled, has been proposed. It is based on making use of the standard tool (mass conservation law), but with the diffusion coefficient, which fulfils the presumption on the dispersive kinetics.

This appears, however, to be not a presumption, but it comes directly from the physics of the process telling us that:
(i) the diffusion coefficient is an inverse power function of the polymer mass, cf. eqs. (3)-(4) [12, 19, 10];
(ii) in typical (say, deterministic [10]) realizations of the process, the mass increases linearly with time $t$, cf. eq. (5) [13, 9, 18, 17, 10].

Point (i) stands for the main assumption of the dispersive ("long-tail") or fractal-like chemical reaction kinetics, for which the probability of return, $P_{ret}$, of the system to its origin scales asymptotically with time $t$, like $P_{ret} \sim t^{-d_s/2}$, and depends upon the spectral dimension of the process [11]. Using elementary knowledge on these kinetics [23], one might even identify our exponent $1 - \frac{1}{D_f}$ as being closely related to the spectral (fracton) dimension, $d_s$, namely, that it is equal to $d_s/2$. Thus, the implications of settling such a physical context, where in fact, many time scales coexist [11, 21], may be quite rich.

It was easy to see that we have introduced a quite powerful mechanism to our modelling. Presuming that we are in a "nearly good" solvent regime, we have taken into
account the following:
(i) the interaction between particles or clusters which do form bigger and bigger objects being eventually absorbed by the crystal or polycrystalline microstructure formed [9] (parameter $\kappa$);
(ii) the geometrical characteristics of the randomly walking objects ("averaged" dimension $d_f$; note that this quantity can also be thought of to remain unchanged in course of time, at least, when measured since a sufficiently mature stage of the growing process [10, 9]).

The most interesting parametric characteristics appears to be, however, the competition parameter \( D_f = d_f/\kappa \), or again, the critical exponent \( 1 - \frac{1}{D_f} \). This characteristics teaches us mostly that the better is the interaction-geometrical adjustment the more effective the polymer crystallization process can be. The best way one can probably see here is to be in the diffusion-controlled regime for the cluster-cluster aggregation process ($\kappa = 1$), and when the polymer chains are rod-like or aligned ($d_f = 1$). This way, some lamellar structures may practically be obtained. Otherwise, we get more or less nonlamellar objects that can reach many other levels of structural (e.g., hexagonal [23]) packings.

Going a bid further, one may ask about the accommodation of segments arriving at the crystal surface, i.e. about the interface-controlled regime of the process in question. This is not explicitly settled in our mechanism, but as a possible natural choice, we would like to propose the random sequential adsorption mechanism, which can, perhaps, be extended to a competition (cooperation) mechanism, between secondary nucleation and polymer accommodation events, taking place at the surface of the growing crystal [24]. It would appear as a result of the crystal surface relaxation [21]. In this case, the growth law (2) should be modified properly, like \( dR/dt = D_eff(1 - \sigma)/p \times (dC/d\tau)_{surf} \), where \( 1 - \sigma \) stands for the coverage of the surface, which in general, can be also a powerly decreasing function of time, where the power contains some information about $k$-mers decorating the crystal surface [24]. This, however, cannot seemingly change the overall time behavior presented for the systems studied, at least, in the late times limit. (By the way, note that in our model the uncoverge $\sigma = 0$, so that a full coverage of the surface was tacidly assumed in the present study.)

Summing up, let us state explicitly that our approach works well within the description of a polymer crystallization (and related, e.g. ordered colloidal or oligomers-containing aggregation phenomena [9, 13]) when the following is guaranteed:
(i) \( D \) used in (1) [3, 2, 14] is the diffusion coefficient of the molecules that diffuse and get stuck to a growing crystal;
(ii) if the diffusing molecules do aggregate in a random manner then relation (6) is fullfilled and, in consequence, \( V' \) does change in time, in the same way as \( D_{eff} \) in eqs. (7) and (8) [10, 16, 12];
(iii) we are in the regime of solvent with positive but rather small excluded volume effect, which ensures at least some nonzero polymer-polymer (or related) attraction.
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