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Trends in polymer physics and theory

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ABSTRACT

We present our personal appraisal of a few recent trends in polymer physics and theory. The four main themes discussed are crystallization and melting of polymers, memory in polymer systems, topologically frustrated polymer dynamics, and phase behavior of polyelectrolyte solutions.

Contents

1. Introduction

The first six decades, since the birth of the "Polymer Hypothesis", have witnessed marvelous accomplishments in terms of characterizing the physical nature of the new class of gigantic molecules accompanied by brilliant theoretical advances, and harnessing amazing physical properties to cultivate the Polymer Age of human civilization. The creativity of human mind to address various fundamental aspects of highly correlated and structured macromolecules was evident through a large body of theoretical and experimental research conducted by many distinguished scientists like Flory, Debye, Stockmayer, Kirkwood, Katchalsky, Zimm, Ferry, Edwards, de Gennes, and so on. The theories and experiments covered almost all essential areas of polymer physics including polymer chain statistics, excluded volume effect, polymer solution thermodynamics, rubber elasticity, polymer dynamics, critical phenomena and phase separation, gels, polyelectrolytes, polymer crystallization, polymer glasses, mapping between polymer chain statistics and field theory, and microphase separation [1–5]. During this classical period of polymer physics, theory and experiments were performed synergistically. Promulgation of closed analytical formulas to be useful in directly comparing with experimental data was the standard practice.

As the polymer field grew more mature, more and more experiments and theories emerged on a variety of fundamental issues in polymer science. Due to the inevitable complexity of issues and perhaps also due to some over-specialization, the connection of the new theories and simulations to experimental systems could be observed not at all instances. The growing extensive literature is beginning to witness a reemergence of quantitative theoretical predictions that are directly pertinent to experimental data, although a significant portion of literature on experiments and simulations leans toward only qualitative picturesque descriptions. Overall, the field of polymer physics and theory is vibrant and very stimulating.

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Nomenclature

D	Diffusion coefficient
F	Helmholtz free energy
F	Random force
I (k)	Normalized scattering intensity at scattering wave vector k
J	Nucleation rate
K	Scattering wave vector
k'_r	Coefficient of electrostatic interaction
k_c	Critical value of scattering wave vector, beyond which fluctuations decay
k_{max}	Scattering wave vector at which fluctuations are at maximum growth rate
k_r	Shift factor for rate of decay due to electrostatic interaction
L	Lamellar thickness
l	Segment length
m	Mass
M	Memory function
r	Spatial position
R_g	Radius of gyration
t	Time
T^0_m	Equilibrium melting temperature
T_c	Crystallization temperature with maximum rate of crystallization
T_m	Melting temperature with maximum rate of melting
T_{melt}	Melt temperature
x	Position of a Brownian particle
Δh	Heat of fusion per unit volume
ΔT	Quench depth
Λ	Period of concentration fluctuations
Ω_k	Rate of growth of fluctuation at wave vector k
χ	Flory-Huggins chi parameter
χ_s	Spinodal value of Flory-Huggins chi parameter
γ	Friction coefficient
κ	Interfacial tension
σ_f	Fold surface free energy
ξ	Average mesh size of a gel
ψ	Order parameter
ψ_k	Order parameter resolved into the scattering wave vector k

In this article, we will present only a few examples of what is new, although the long-standing challenge of understanding polymer glasses is still being pursued. Our examples include (1) Entropic barriers in polymer crystallization and melting, (2) Polymer memory, (3) Topologically frustrated dynamics, and (4) Phase behavior of polyelectrolyte solutions, with a special mention of polarizability.

Naturally, the above examples are not the only ones requiring detailed discussions, but are chosen in order to illustrate the generality of the underlying physics applicable to a diverse set of specific problems, and in view of the technical challenges in each of these examples.

2. Examples of ongoing challenges and trends

2.1. Entropic barriers in polymer crystallization and melting

As vividly exhibited by many experimental results over the past seven decades, crystallization and melting behaviors of polymers are extremely complex [6,1–14]. An adequate understanding of the phenomenology of polymer crystallization/melting is still elusive,

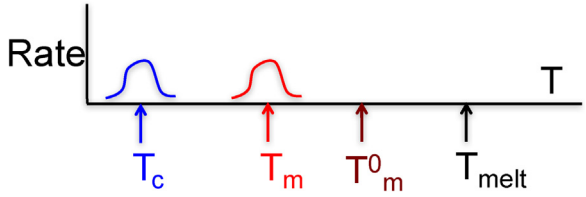

Fig. 1. Definition of crystallization temperature T_c, melting temperature T_m, equilibrium melting temperature T^0_m, and melt temperature T_{melt}. The ordinate denotes the rate of crystallization (blue) around T_c and melting (red) around T_m. These distribution of rates are only cartoons.

due to the interplay between conformational entropy of chains opposing order and the short-range attraction among polymer segments favoring order. Only recently, the significance of having to have finite entropy at non-zero temperatures has been recognized, which translates into the semicrystalline state being the equilibrium state instead of the classical paradigm that fully extended chain state is the equilibrium state at finite temperatures [15]. Even so, what is the equilibrium melting temperature for polymers? This is not yet known.

For a small molecular system, crystallization and melting occur at a specific equilibrium melting temperature. In contrast, the crystallization of a polymer melt occurs only at temperatures substantially lower than the anticipated equilibrium melting temperature $T_m{}^0$ (Fig. 1), and the crystalline state is a hierarchical assembly of lamellae with amorphous regions in between the lamellae. The crystallization rate is broadly distributed at these crystallization temperatures and the temperature of maximum crystallization rate is marked as the crystallization temperature T_c (Fig. 1). When the crystallized polymer at T_c is heated, it eventually melts. Sometimes, the lamellae can thicken during the melting process, resulting in recrystallization during melting. The melting temperature is also characterized by a broad range, and even the definition of melting temperature T_m (Fig. 1) is not unique. After melting at T_m, the system is kept at a higher melt temperature T_{melt} (Fig. 1) for certain annealing time. When this melt is recrystallized, the kinetics of the second crystallization is accompanied by significant memory effects [16–20].

The interplay between T_c, T_m, $T_m{}^0$, and T_{melt} and its manifestation in crystallization, melting, recrystallization, and crystallization memory are not fully understood and progress is being made in this effort using theory and simulations. In contrast with the traditional approaches for crystallization, the recent approaches emphasize the importance of conformational entropy of polymer chains at crystallization temperatures.

Historically, the melting temperature of polymer crystals has been interpreted using the Gibbs-Thomson (GT) equation, derived based on the condition of thermodynamic equilibrium. Assuming that GT equation is valid also for non-equilibrium lamellae, the Hoffman-Weeks plot was constructed allowing for crystal thickening to extrapolate the equilibrium melting temperature. Neither Gibbs-Thomson law nor Hoffman-Weeks plot has been found to fit self-consistently with experimental observations [21]. According to the GT law, the relation between the melting temperature and equilibrium melting temperature is given by

$$T_m = T_m^0\left(1 - \frac{2\sigma_f}{L\Delta h}\right) \tag{1}$$

where L is the lamellar thickness, σ_f is the fold surface free energy per unit area, and Δh is the heat of fusion per unit volume. In view of the thermodynamic stability of semicrystalline state, due to contributions from conformational entropy of ties, loops, and tails in amorphous regions, a substitute of the above Gibbs-Thomson

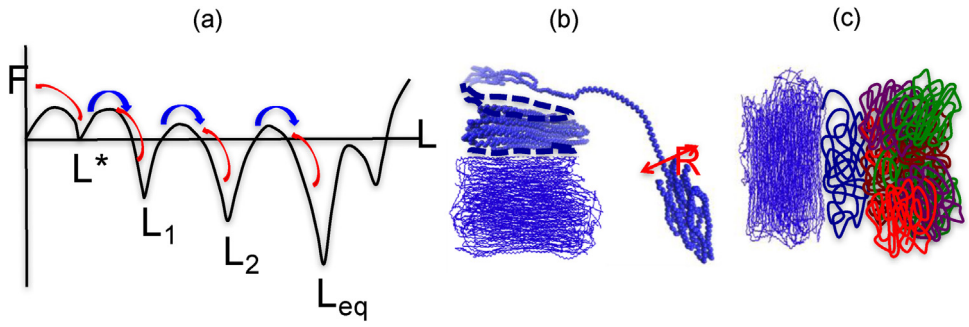

Fig. 2. (a) Free energy landscape for crystallization and melting. (b) Melting by fragmentation; R denotes the lateral dimension of a typical fragment. (c) Sequential peeling off of chains during melting, but faced with an entropic barrier for comingling with the melt.

law is required which should depend on the equilibrium lamellar thickness L_{eq}.

The kinetics of crystallization and melting is also challenging and is being actively investigated using new ideas. The free energy landscape for polymer crystallization is now well recognized to involve multiple entropic barriers sketched in Fig. 2a [22]. Once the initial lamella is born with thickness L*, it thickens to L_1, L_2, etc., by crossing the intervening entropic barriers in a sequential manner until the equilibrium thickness L_{eq} is reached (as shown by the blue arrows in Fig. 2a). At the same time, the lamellar thickness can also fall back to the initial thickness by a series of barrier hopping as indicated by the red arrows in Fig. 2a. The net result of these competing processes is recrystallization which is responsible for lamellar thickening during melting. When the temperature is high enough the processes denoted by the red arrows in Fig. 2a become more favorable and a description of kinetics of melting would ensue. An approach based on multiple barriers with collective behavior of the whole system looks promising and represents a general scenario common to several challenging polymer problems.

Instead of step-wise melting cartooned in Fig. 2a, the melting process can follow an entirely different free energy landscape from that of crystallization, as shown in Fig. 2b and c. In Fig. 2a, the lamellae can fragment with the resultant fragments acting as nuclei for recrystallization. In Fig. 2c, the chain segments can peel off sequentially but are unable to immediately interpenetrate into the entangled chains in front of the crystal-melt interface. This is equivalent to a creation of an entropic barrier for melting. A theoretical framework to describe the various scenarios depicted in Fig. 2 is needed to explain the current knowledge from an enormous set of experiments.

2.2. Polymer memory

Memory is a natural attribute of polymer systems, ranging from single macromolecule to gels, glasses and crystals. The origin of memory in polymer systems lies in the inevitable arrest of many conformational states of polymers away from ergodicity at finite times allowed for the polymers. As an example of molecular memory, when a RNA molecule is titrated as a function of lowering pH, the RNA conformations change in a pathway which is different from the pathway for the reverse process of increasing pH. As an example of macroscopic memory in polymer systems, we may consider the polymer crystallization process described in the above section, where it is known as melt-memory.

The melt-memory is a common phenomenon in polymer crystallization where recrystallization of a molten semicrystalline polymer or a dissolved polymer in a solvent depends profoundly on the initial disordered state. Despite the knowledge from beautiful experiments conducted over several decades [16–20], the physics and theory of melt-memory is beginning to receive attention only recently. Basically, when a polymer system is heated above their nominal melting temperature to a disordered state without any reminiscence of even local order, and then cooled to undergo crystallization, the new crystallization temperature and morphological details depend on the temperature of the disordered state. This phenomenon defies the major theme of nucleation and growth where it is the distance in temperature away from the equilibrium melting temperature that is relevant to describe crystallization. Instead, the distance in temperature from the melt temperature and the shelf life of the system in the disordered state dictate the crystallization process. The conventional practice that the nucleation rate J is dictated by the quench depth $\Delta T \equiv T_m^0 - T_c$,

$$J \sim \exp\left(-\frac{A}{T(\Delta T)^{\alpha}}\right) \tag{2}$$

is not valid in the presence of memory effects. Here A is related to heat of fusion and α depends on the space dimension. Instead, $T_{melt} - T_c \equiv \Delta T^* + \Delta T$ dictates the crystallization kinetics. ΔT^* can be either negative ($T_{melt} < T_m^0$) or positive ($T_{melt} > T_m^0$). The phenomenology of melt-memory strongly suggests that there must be an interlude of at least one intermediate inhomogeneous melt state in the pathway between the completely homogenized melt state and the crystalline state that would eventually form at T_c.

Theoretical attempts to formalize the above ideas just have begun. In one attempt [23], the intermediate state can arise from local orientational ordering of chain segments analogous to the smectic pearl-like baby crystals which are strung together topologically by chain connectivity (Fig. 3a). The generic free energy landscape at temperatures below T_m^0 that includes this intermediate state is cartooned in Fig. 3b, where the abscissa denotes the degree of crystallinity and i, m, and f denote the initial, metastable, and final states. There are two barriers in the crystallization process, capturing the melt-memory effects. This kind of theory of melt-memory is only at its early stage of development and understanding of the rich phenomenology of melt-memory and the related memory effects in polymer glasses is at the forefront of theoretical challenge.

2.3. Topologically frustrated dynamics

Diffusion and drift of electrons, ions, guest macromolecules inside a polymer gel or a polymer melt have attracted considerable recent interest, in view of potential applications in solar energy, batteries, memory devices and more efficient separation technologies [24–28]. The fundamental challenge arises from the topological correlations of the polymer matrix in the case of electrons and ions, and from the topological correlations among the guest macromolecules and the host matrix in the case of macromolecular analytes, as illustrated in Fig. 4. In Fig. 4a, either an electron or an ion hops around inside the polymer matrix by cross-

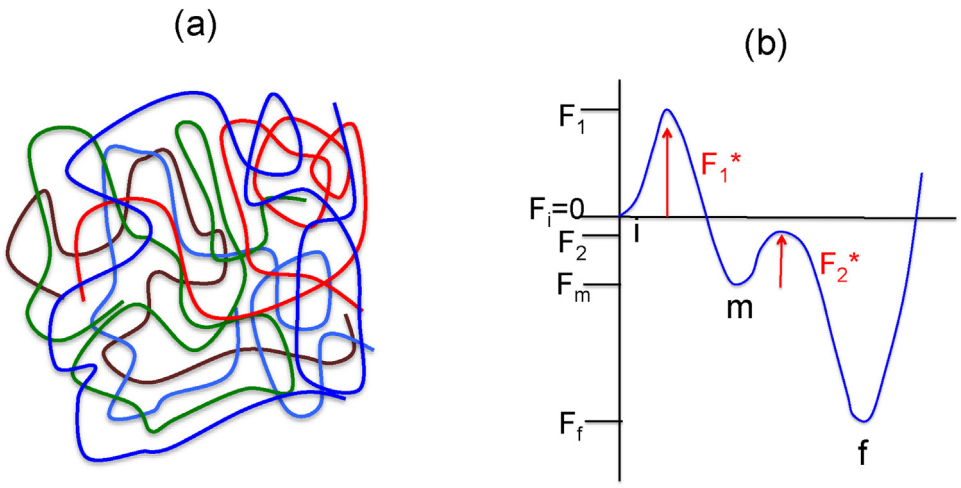

Fig. 3. (a) Cartoon of an intermediate state with local orientational order. (b) Free energy landscape versus degree of crystallinity with an intermediate metastable state intervening the initial molten state and the final semicrystalline state.

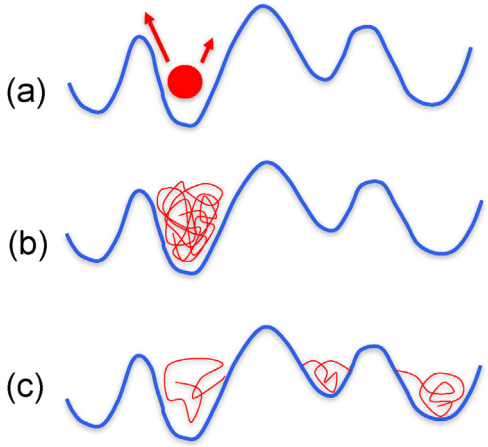

Fig. 4. (a) An electron or an ion hops through a series of free energy barriers created by the host polymer matrix. (b) A single macromolecule captured inside one free energy minimum undergoes diffusion through multiple entropic barriers one at a time. (c) A single macromolecule trapped inside many correlated free energy wells gets frustrated for diffusion through multiple correlated barriers.

ing many free energy barriers situated at various spatial locations due to the inherent structural heterogeneity of the matrix. This results in highly correlated slaved diffusion of the electron or ion. Presence of externally imposed forces, responsible for the drift of the electron or ion, tilts the free energy landscape in specific ways and the slaved diffusion is further frustrated by the tilted free energy landscape.

As a general description, the dynamics of the electron or ion in such a topologically correlated environment can be described using a memory function $M(t-t')$ for the Langevin equation for the time (t) evolution of the position (x) of the particle as

$$m\ddot{x}+\gamma\dot{x}+\int dt' M(t-t')\dot{x}(t')=f(t) \tag{3}$$

where m is the mass, γ is the friction coefficient, and f is the random noise. Instead of the spatial position, any suitable order parameter can be denoted by the variable x. The task is to derive the memory function that is appropriate for the particular system and use the standard methodologies in statistical physics, such as mode-mode coupling, continued fraction, etc., to describe the slaved drift-diffusion.

If the guest particle is a macromolecule as in Fig. 4b, the guest molecule is itself topologically correlated and is subjected to additional correlation created by the various free energy barriers. Such a scenario emerges in the phenomenon of polymer translocation [29], where a single macromolecule in salty water is threaded through a narrow nanopore under an electric field as a single file. The presence of chemical patterns on the nanopore creates highly corrugated free energy landscape for polymer translocation. Successful theories to describe this scenario are based on the entropic barrier formalism and has led to significant insight into the relation between polymer translocation and the nucleation-and-growth process in any ordering process.

The third situation, as described in Fig. 4c, corresponds to conditions where even one guest macromolecule is so large that it can occupy several free energy wells of the free energy landscape at any time. This leads to highly correlated polymer dynamics as an amplification of mutual topological correlation between the guest macromolecule and the host polymer system. It is conceivable that the large scale conformations of such trapped macromolecules could be used for storage of conformational memory [30].

From an experimental point of view, the multiple barriers from the host matrix can be created by choosing the matrix as a gel where the polymer strands can hold chemical patterns and the spatial heterogeneity can be varied with its mesh size. The dynamics of a guest macromolecule corresponding to the above three situations is sketched in Fig. 5. If the size of the macromolecule (represented by its radius of gyration R_g) is very small compared to the mesh size ξ of the gel, then the dynamics is described by the well-known sieving mechanism. When R_g becomes comparable to ξ, the entropic barrier dynamics description for polymer translocation mentioned above becomes applicable. In fact, this mechanism is a crossover description between the Rouse dynamics in semidilute solutions and the reptation dynamics expected for highly concentrated solutions or melts. In the asymptotic limit of $R_g \gg \xi \sim l$, where l is the segment length, reptation dynamics is valid. In this limit, each valley in Fig. 4c holds essentially only one segment. On the other hand, if a large number of segments were to reside in each of the valleys occupied by a single macromolecule, such that $R_g \gg \xi > l$, a new dynamical regime may be expected, as indicated by the thick arrow in Fig. 5. Here, the chain cannot undergo diffusion under ambient conditions, since for this to occur the chain has to navigate simultaneously through multiple entropic barriers which are strongly correlated. Such a scenario would result in a hierarchy of local dynamics reflecting the heterogeneity in the mesh size of the host gel, and consequently exhibit a heavily stretched expo-

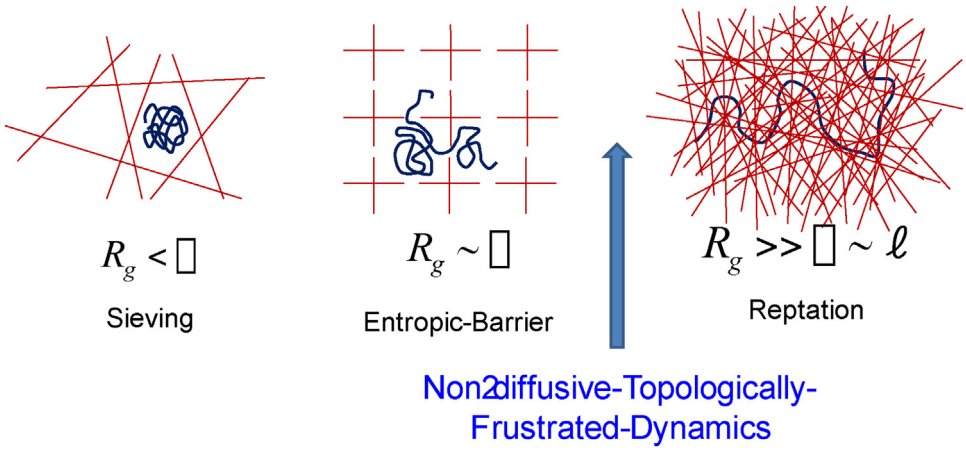

Fig. 5. Emergence of a new regime of non-diffusive topologically frustrated dynamics intervening the entropic barrier model and reptation model. For very low confinements, the sieving model is operative.

nential decay with time for various correlation functions of the chain dynamics. In fact, recent experiments demonstrate the emergence of this new non-diffusive topologically frustrated dynamical regime intervening the entropic barrier regime and the reptation regime [30]. These arguments bring fresh questions on how to compute the magnitude of entropic barriers and formulate a predictive theory for topologically correlated systems.

2.4. Phase behavior of polyelectrolyte solutions

The phase behavior of polyelectrolyte solutions has recently attracted much attention, primarily due to the importance of the coacervate phase formed by liquid-liquid phase separation in solutions containing oppositely charged polyelectrolytes [31–33]. Even without the complications arising from complexation between oppositely charged chains to form dipolar aggregates, the phase behavior of polyelectrolyte solutions remains as a continuing challenge for a full understanding. Although the experimental data on polyelectrolyte phase behavior are known for more than six decades [34,35], there has not been a good theory so far, unlike the Flory-Huggins theory for uncharged systems. The primary reason for the challenge is the specificity of the counterions and the electrolyte ions in the solution. This in turn is related to the polarizability of the ions and the medium [36–39]. Until an adequate theory for the polarizability of solutions of charged macromolecules is formulated, the phase behavior of such solutions will remain as a challenge for understanding.

While the mechanism of liquid-liquid phase separation in solutions of uncharged macromolecules is quite well understood in terms of spinodal decomposition and nucleation-and-growth, the kinetics of phase separation in polyelectrolyte solutions is essentially a new territory to explore. From a theoretical point of view, it is necessary to formulate a theory of interfacial tension where the combined effects of long-range electrostatic interactions and topological correlations are present. Also, expressions for the Onsager coefficient describing the transport of charged macromolecules and other couple ions in the solution are yet to be derived.

Even from a coarse-grained outlook, the kinetics of phase separation in polyelectrolyte solutions appears to be qualitatively different from what we know in uncharged solutions and blends. As an example for uncharged systems, consider the mechanism of spinodal decomposition. The concentration φ of polymer in a two-component system, defined through the order parameter $\psi = \phi - \phi_c$ (ϕ_c being the critical concentration) fluctuates in space (Fig. 6a). The spacing between domains of higher concentration, $\Lambda = 2\pi/k$ (k is the scattering wave vector), increases with time. The standard Flory-Huggins theory of solutions gives the following equation for free energy F of the solution,

$$\frac{F}{k_B T} = \frac{1}{2}\sum_k (A + \kappa k^2)\psi_k^2 \tag{4}$$

where κ is related to the interfacial tension and A is related to the quench depth in temperature as

$$A = 2(\chi_s - \chi) \tag{5}$$

with χ being the Flory-Huggins parameter and χ_s its value at the spinodal point. The time evolution is given by

$$\frac{\partial \psi_k}{\partial t} = -Dk^2 \frac{\delta F}{\delta \psi} \tag{6}$$

where D is the diffusion coefficient of the polymer. Combining the above equations, the normalized scattering intensity in the very early stage of spinodal decomposition is given by

$$I(k) = e^{2\Omega_k t} \tag{7}$$

With

$$\Omega_k = -Dk^2\left(A + \kappa k^2\right) \tag{8}$$

The rate of exponential growth of intensity depends on the scattering wave vector, as sketched in Fig. 6b. The fluctuations with wave vectors smaller than k_c(given in the figure) grow and those with $k > k_c$ decay. The maximum intensity is at k_{max} as indicated in the figure.

For polyelectrolyte solutions, the free energy expression at the mean field level is

$$\frac{F}{k_B T} = \frac{1}{2}\sum_k (A + \kappa k^2 + \frac{k'_r}{k^2})\psi_k^2 \tag{9}$$

where the last term inside the parenthesis is due to long-range electrostatic interactions. The direct consequence of this term on the kinetics of spinodal decomposition is

$$\frac{\partial \psi_k}{\partial t} = -Dk^2\left(A + \kappa k^2\right)\psi_k - k_r \psi_k \tag{10}$$

where $k_r = D\, k'_r$. The initial rate of growth of composition fluctuations follows from the above equation as

$$\Omega_k = -Dk^2\left(A + \kappa k^2\right) - k_r \tag{11}$$

Now the rate is shifted down by a constant amount k_r, as sketched in Fig. 6c. Therefore, for polyelectrolyte solutions, we expect that only fluctuations with only intermediate wave lengths,

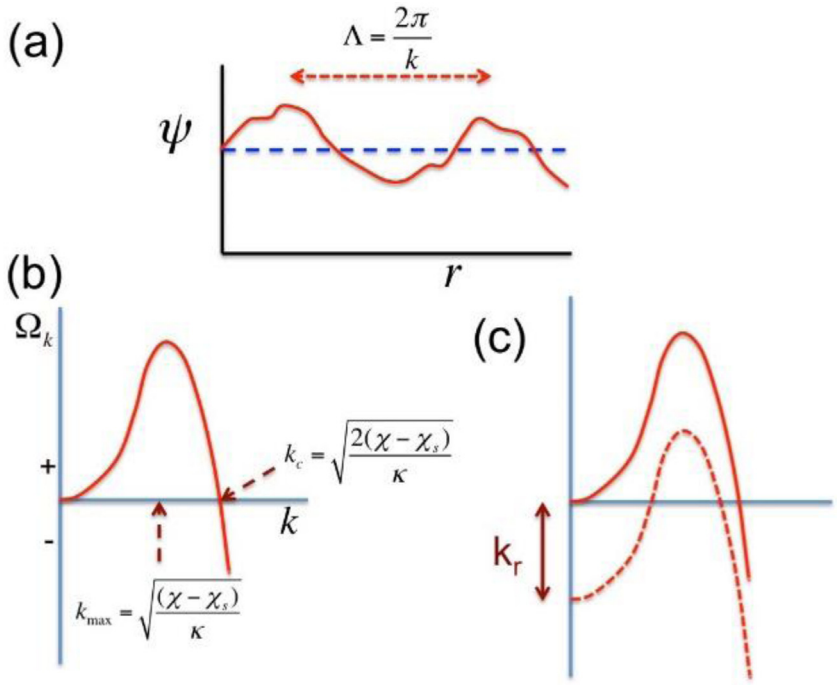

Fig. 6. (a) Sketch of composition fluctuations. (b) For uncharged polymer solutions, fluctuations larger than one cutoff size grow with time. (c) For polyelectrolyte solutions (shown by the dashed curve), only fluctuations with intermediate size, with two cutoffs, will grow with time and consequently will generate periodic patterns in liquid-liquid phase separation.

defined by the two cutoff values of k are allowed instead of all fluctuations beyond a certain size that would occur for uncharged solutions. As a result, we expect some periodic patterns in the evolution of morphology of polyelectrolyte solutions undergoing liquid-liquid phase separation.

In addition to the above expectation, there could be an additional complication arising from the formation of counterion-mediated dipolar aggregates even in the homogeneous phase of polyelectrolyte solutions, as evidenced in the slow mode of diffusion [40]. These aggregates might persist when the solution is quenched from a homogeneous solution to a phase separating solution and might template the spinodal decomposition mechanism as well as the nucleation-and-growth process. In addition, there is the omnipresent polarizability effects which are specific to the various ions and the chemical details of the polymer chains in the solution. Almost all of polyelectrolyte effects seem to boil down to the polarizability of the medium, which might profitably be gleamed through impedance spectroscopy.

3. Conclusions

A brief personal view of the current trend and future challenges in polymer physics and theory is given. Only time will tell whether the issues mentioned in this article are indeed the current trend or not. Nevertheless, it is hoped that the reader would find the items described here to be of interest.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

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