Macromolecules assume compact conformations in certain situations. Examples include DNA in living cells, proteins in native states and other polymers in poor solvent conditions or under a compression field. Once released from the condition, these polymers expand to swollen coiled state, which is characterized by developed fluctuations. This expansion process is of interest in two different contexts. First, this process is relevant to coil-globule transitions, thus, regarded as a fundamental topic in polymer science [1, 2]. Unfortunately, there are comparatively fewer past studies on this expansion process than on the folding (coil to globule) process. [3, 4, 5], [6, 7, 8, 9, 10, 11, 12]. The aim of the present Letter is to provide a unified framework to facilitate a number of potential applications in biological manipulations and observe individual polymers, thereby facilitating a number of potential applications in biological as well as nanoscale sciences [7, 8, 9, 10, 11, 12]. The second case of interest is encountered in the field of confined polymers [6]. A recent advance in nanoscale fabrications and single-chain experiments allows one to manipulate and observe individual polymers, thereby facilitating a number of potential applications in biological as well as nanoscale sciences [7, 8, 9, 10, 11, 12]. The aim of the present Letter is to provide a unified framework to describe decompression processes engaged in such situations.

Naively, the problem is analogous to the diffusion of molecular gases, which are initially confined in a finite-size box. For our case, the essential difference from this simple example lies in the connectivity of monomeric units into a string, in which a small entropy does not play any major role. By taking such polymeric natures correctly into account, it is naturally formulated as a nonlinear diffusion problem, which serves as a basis for various decompression processes such as (i) the expansion, i.e., unfolding, and (ii) the ejection of a geometrically compressed polymer from a narrow pore (Fig. 1).

In the case of polymer expansion (case (i)), a symmetry allows for an analytic solution. However, this is a rather special case, and the nonlinearity in the partial differential equation usually requires a numerical calculation. In such a case, we propose a scheme uniform approximation, in which the nonuniformity of the segment distribution is totally neglected. It allows one to obtain an approximate solution easily, which can yet be reasonably compared with the exact solution, provided that mechanisms of the driving force and the dissipation are correctly identified. We apply this scheme to the case of polymer ejection (case (ii)) and demonstrate a very good agreement with the numerical simulations reported so far.

Consider a compressed globular chain, the size $R_0$ of which is substantially smaller than the relaxed size $R_F = aN_0^\nu$ in bulk ($a, N_0$ are the size, the number of monomers and $\nu$ is the Flory exponent). The corresponding average volume fraction $\phi_0 \simeq N_0a^3/R_0^3 \ll 1$ is assumed to be small. Here and in what follows, we assume that isotropic compression, i.e., in a sphere, but generalization to anisotropic compression is straightforward. When given an escaping route, the polymer starts to be decompressed toward the relaxed coil. The time evolution of volume fraction $\phi(r)$ obeys the continuity equation: $\partial \phi(r)/\partial t = -\nabla \cdot j(r)$ with the flux $j(r) = -L(r)\nabla \mu(r)/\phi(r)$. In order to obtain the chemical potential $\mu(r) = \partial f(r)/\partial \phi(r)$ and the transport coefficient $L(r)$, we utilize the fact that the compressed polymer resembles a semidilute solution, which amounts to say that the compressed polymer is viewed as a dense piling of blobs of size $\xi(r) \simeq a\phi(r)^{\nu/(1-3\nu)}$. Such a situation is called a strong confinement (SC) in Refs. [13, 14] (see also eq. (5)). Then, the excess free energy density due to the compression and the dissipation mechanism are, respectively, evaluated by assigning $\sim k_B T$ (thermal energy) and the Stokes friction per blob [15]: $f(r) \simeq k_B T/\xi(r)^3$ and $L(r) \simeq g(r)/(\eta \xi(r))$ where $\eta$ is the solu-
tion viscosity and $g$ is the number of monomers per blob ($\xi \simeq a g$). This leads to $j = -a^2/\tau_0 \phi(r) \nabla \phi(r)$ with the monomer scale time constant $\tau_0 \simeq \eta a^3/(k_B T)$. The same expression is obtained from slightly different route, which utilizes the semidilute solution analogy in a more transparent way: $j = -D_c(\tau) \nabla \phi(r)$, where $D_c(\tau) \simeq k_B T/(\eta \xi(r))$ is the cooperative diffusion coefficient [13]. Using this flux and the continuity equation, we arrive at the following:

$$\partial_t \phi = \left( a^2/\tau_0 \right) \nabla \left[ \left( \phi(r) \right)^m \nabla \phi(r) \right], \quad (1)$$

with $m = \nu/(3\nu - 1)$ [28]. This equation constitutes a basis for the decompression process and should be solved with appropriate initial and boundary conditions specified for each case of interest.

**a. Expansion and unfolding** There are several ways to achieve decompression. The simplest is to switch off the external compression field abruptly at $t = 0$. Then, the polymer will expand isotropically toward the relaxed coil (Fig. 1). In the context of the unfolding by the temperature (more generally, solvent quality) jump across the $\theta$ temperature ($T_{ini} \to T_{fin}$), the initial compact state can be viewed as a dense piling of thermal blobs of size $\xi_{th} = a/|\phi(0)| = a g_{th}^{1/2}$, where $z = (T - \theta)/\theta$ is the reduced temperature. Hence, the initial size of the polymer is $R_0 \simeq \xi_{th}(N_0 / g_{th})^{1/3} = a N_0^{1/3}/|\phi_{ini}|^{1/3}$.

Let us first make eq. (1) dimensionless by introducing a scaled coordinate (radial component) $\tilde{r} = r/R_F$, volume fraction $\tilde{\phi}(\tilde{r}) = \phi(r)/\phi_F$ and time $\tilde{t} = t/\tau$, where $\phi_F = a^3 N_0 / R_F^3$ denotes the monomer volume fraction in a relaxed state. By setting the time unit $\tau = \tau_{ex} = \tau_0 N_0^{3\nu}$, we can rewrite eq. (1) as

$$\partial_{\tilde{t}} \tilde{\phi}(\tilde{r}) = \tilde{r}^{-2} \partial_{\tilde{r}} \left[ \tilde{r}^2 \tilde{\phi}(\tilde{r})^m \partial_{\tilde{r}} \tilde{\phi}(\tilde{r}) \right], \quad (2)$$

The characteristic time for expansion $\tau_{ex}$ depends only on the relaxed coil size $R_F$ and not on the initial size. Therefore, it has the same scaling form as the longest relaxation time in the relaxed state. The solution reads [23]

$$\tilde{\phi}(\tilde{r}, \tilde{t}) = c_0 \tilde{R}(\tilde{t})^{-3} \left[ 1 - \left( \tilde{r}/\tilde{R}(\tilde{t}) \right)^2 \right]^{1/m}, \quad (3)$$

where $c_0 = \Gamma [5/2 + 1/m] / (\pi^{3/2} \Gamma (1/m + 1))$ with the Gamma function, $\Gamma$, is the normalization factor and $\tilde{R}$ corresponds to the overall chain size, which evolves according to

$$\tilde{R}(\tilde{t}) = \tilde{R}_0 \left[ 1 + \tilde{t}/\tilde{t}_{ini} \right]^{\alpha_0 \nu}, \quad (4)$$

with the exponent $\alpha_0 = (3\nu - 1)/(9\nu - 2)$ and the time constant $\tilde{t}_{ini}^{(0)} = \alpha_0 m R_0^{2/\alpha_0} / (2 c_0^m)$. Plots of the solution are shown in Fig. 2 along with the results of numerical calculation carried out using the initial condition of a step-like distribution. In the strict sense, solution (3) is valid only for the initial condition $\phi(0) = c_0 \tilde{R}_0^{-3} [1 - (\tilde{r}/\tilde{R}_0)^2]^{1/m}$. Nevertheless, the figure shows that the dependence on the initial distribution is not significant. The analytical results correspond well with those of the numerical calculation, particularly for the mean size of a chain $\tilde{R}_m$.

$$\tilde{R}_m(\tilde{t}) \equiv \int \tilde{r} \tilde{\phi}(\tilde{r}) d\tilde{r} / \int \tilde{\phi}(\tilde{r}) d\tilde{r} \simeq \tilde{R}(\tilde{t}), \quad (5)$$

A nonlinear dependence on the chain length: $\Delta F \sim N_0^{3/4}$ for a chain with $\nu = 3/5$ (in good solvent) and $\Delta F \sim N_0^1$ with $\nu = 1/2$ (in theta solvent) is a characteristic of the SC regime [13, 14]. By noting the velocity gradient $\nabla v \simeq \xi(t) / \tilde{t}(t)$, the overall dissipation is evaluated as

$$T \dot{S}(t) \simeq \eta R(t) \dot{R}(t)^2. \quad (6)$$

Balancing the rate of the free energy change and the dissipation, we obtain the following solution

$$\Delta \hat{F}(\dot{t}) = -T \dot{S}(t) \Leftrightarrow \dot{R}(t) = R_0 \left( 1 + t/\tau_{ini} \right)^{\alpha}, \quad (7)$$

with the exponent $\alpha = (3\nu - 1)/(9\nu)$ and a time scale $\tau_{ini} = \tau_0 (R_0/a N_0^{1/3})^{1/\alpha}$. Again, this can be rescaled with the characteristic time $\tau_{ex}$ so that we obtain the same form as in eq. (4): $\tilde{R}(\tilde{t}) = R(t)/R_F = \tilde{R}(1 + \tilde{t}/\tilde{t}_{ini})^{\alpha}$ with the rescaled time $\tilde{t}_{ini} = \tilde{t}_{ini}/\tau_{ex} = (\tilde{R}_0)^{1/\alpha}$. This time $\tilde{t}_{ini}$ designates an initial transient period, which depends on the degree of the initial compression $C_{com} \equiv$
the chemical potential $\Delta F_0 = C_\text{com}^{3 \nu/(1 - 3 \nu)}$. At $\tilde{t} > \tilde{t}_\text{int}$, a sub-diffusion like scaling regime $\tilde{R}(t) \approx \tilde{t}^\nu$ follows. All these results agree reasonably well with the exact solution except for a slight difference in the dynamic exponent. In particular, the uniform approximation is able to predict the correct characteristic time $\tau_x$ of expansion. This success traces back to the correct evaluation of the driving and dissipation mechanisms based on the fundamental length scale $\xi$.

c. Ejection Consider a long polymer initially confined in a spherical cavity of size $R_0$. Through a small hole (with a size comparable to that of monomers), the polymer escapes (Fig. 1). This process of polymer ejection, i.e., a polymeric version of effusion, has recently attracted considerable attention inspired by the biological problem such as a DNA packed into and unpacked out of a phage capsid. From a fundamental point of view, there have also been many theoretical and numerical attempts to understand how a flexible chain is ejected from a pore [10] [17] [18]. Even in this simplest setup, however, the situation is yet controversial. It was reported in the most recent works criticized eq. (8) by the use of the Monte Carlo simulation [18]; one of the latest works criticized eq. (8) by the use of the Monte Carlo simulation [18]. Even in this simplest setup, however, the situation is yet controversial. It was reported that the Monte Carlo estimate of the ejection time $\tau_{ej}$ can be fit well by the formula

$$\tau_{ej}^{(D)} \sim N_0 (N_0 / \phi_0)^{1/3}$$

which may be obtained by assuming $\Delta F \simeq \Delta F_{\text{ideal}} \sim N_0$ [17]. One of the latest works criticized eq. (8) by emphasizing the importance of the notion of SC, and proposed the following formula based on the systematic Monte Carlo simulation [18]:

$$\tau_{ej}^{(m)} \sim N_0^{1+\nu} / \Delta \mu \sim N_0^{1+\nu} \phi_0^{1/(1-3\nu)}$$

where $\Delta \mu = \Delta F / N_0$ is the free energy of the confinement (eq. (5)) per monomer, i.e., the chemical potential difference as a driving force. However, the origin of this scaling is unclear. Indeed, it was proposed as a translocation time of a polymer driven by strong and constant $\Delta \nu$, where the second near-equality holds in the limit of the strong driving force [21]. In the present case of the ejection, $\Delta \mu$ is far below such an asymptote and gradually decreases with the process advanced. Moreover, eq. (5) shows an unexpected opposite trend of the chain-length dependence for polymers in good and $\theta$ solvent: $\tau_{ej}^{(m)} \sim N_0^{3/20}$ for $\nu = 3/5$ and $\tau_{ej}^{(m)} \sim N_0^{-1/2}$ for $\nu = 1/2$. In such a situation, it is pertinent to go beyond the scaling formula and to clarify the underlying physics.

In principle, one can numerically solve eq. (1) with the boundary condition ensuring a vanishing flux at the wall except for the pore region. Here, we shall apply the method of uniform approximation to gain useful insight. The free energy is essentially the same as that in eq. (5), but now the dynamical variable is the number of monomers $N(t)$ left inside the cavity, while the cavity size $R_0$ remains constant: $\Delta F / (k_B T) \simeq (a/R_0)^{3\nu/(3\nu - 1)} N(t)^{3\nu/(3\nu - 1)}$. At a particular moment during the ejection, only the monomer residing at the pore feels a resultant osmotic driving force $\sim k_B T / \xi(t)$. This affects the other monomers yet interior cavity, which would be quantified by a distance dependent response function. A linear response theory then connects the response to the correlation function of the concentration fluctuation. This consideration indicates that the overall dissipation is dominated by the proximity of the pore within the range of the correlation length $\xi(t)$, where there exists a velocity gradient of segments of the order $a N(t) / \xi(t)$. Therefore, the dissipation term is evaluated as $T \dot{S}(t) \approx q \left( \dot{N}(t) a / \xi(t) \right)^2 \xi(t)^3$.

The time evolution is obtained as

$$\Delta \tilde{F}(t) = -T \dot{S}(t) \rightleftharpoons N(t) = N_0 (1 + t/\tau)$$

with the exponent $\beta = (1 - 3\nu) / (2(1 - \nu))$ and time constant $\tau_1 \approx \tau_0 \phi_0^{(1+\nu)/(1-3\nu)} N_0$. The dynamic feature in eq. (10) is quite similar to the recent result of the stochastic rotation dynamic simulation [19]. This osmotic driven process ceases at $\tau_2$ that is determined by $N(t) \tau_0 \approx \tau_1.2 \equiv \tau_1 + \tau_2 = \tau_0 \phi_0^{(\nu+2)/(3\nu)} N_0^{(\nu+2)/(3\nu)}$, in which $\tau_0 \approx (R_0/a)^{1/\nu}$ is the number of monomers corresponding to the relaxed chain size $R_0$. After $\tau_2$, there is no driving force, and the chain diffusively escapes from the cavity, which takes a time $\tau_D \approx R_0^2 / N_0$, with the diffusion coefficient $D_\text{N}$ of the polymer. Thus, we arrive at the formula for the total ejection time $\tau_{ej} = \tau_2 + \tau_D \approx \tau_1.2 + \tau_D$, where the second near-equality holds in the situation of our interest, i.e., $F \gg R_0$.

Let us see how this can be compared with previous simulations. We note that $\tau_{ej}$ was so far measured in a model system in which the effect of the induced flow of solvent, i.e., hydrodynamic interactions, was neglected. To cope with this situation, we need to modify the dissipation term as $T \dot{S}(t) \approx q a^2 N(t)^2 g(t)$. This modification changes the dynamic exponent to $\beta = (1 - 3\nu) / (3(1 - \nu))$ and time constant $\tau_1 \approx \tau_0 \phi_0^{2(1-3\nu) N_0^{1-3\nu}}$. Identifying the diffusion coefficient as $D_\text{N} \approx k_B T / (\eta_0 a N_0)$, the diffusion time is evaluated as $\tau_D \approx \tau_0 \phi_0 2^{-3/2} N_0^{3/3}$. In the limit of strong compression $R_0 \ll R_F$ with large $N_0$ and $R_0$, $\tau_{ej}$ asymptotically approaches the simple scaling form $\tau_{ej} \approx \tau_0 (R_0/a)^{3/2}$ with no dependence on $N_0$. However, in most practical situations, the two contributions $\tau_1.2$ and $\tau_D$ are mixed. Analyzing various reported data in terms of our formula strongly indicates that the result in ref. [17] (with small $N_0$ and $R_0$) corresponds to the late-stage diffusion dominated regime. In contrast, ref. [18] employing larger $N_0$ and $R_0$ most probably monitors the mixing of the driven-ejection and diffusion regimes. The asymptotic regime is realized only for extremely long chains. Examples of the analysis (with $\nu = 3/5$) are shown in Fig. 3, in which the dependence of $\tau_{ej}$ on $R_0$ shows a clear crossover from the diffusion dominated regime $\tau_{ej} \approx \tau_2 \approx R_0^0$, whose scaling form is close to eq. (8) to the asymptotic $\tau_{ej} \approx \tau_1.2 \approx R_0^0$, between which there is a region where eq. (9): $\tau_{ej} \sim R_0^{15/4}$ looks valid. In addition, scaling plots of reported eje-
FIG. 3: Comparison of predicted ejection time with that obtained from previous numerical experiments. (a) Double log-log plot of $\tau_{ej}$ as a function of $R_0$ for various system sizes. (b) Scaling plot of $\tau_{ej}$ vs. $\tau_D$ for small systems. (c) Scaling plot of $\tau_{ej}$ vs. $\tau_{1,2} + \tau_D$ for intermediate systems. Numerical data of $\tau_{ej}$ in (b) and (c) were extracted from [17] and [13], respectively.

tion times provide more concrete evidence that ref. [17] and ref. [18], respectively, monitor the ejection processes in the small and intermediate size systems in accordance with the above scenario. We obtain very good data collapse without any fitting parameters (Fig. 3b and c) [27]. This supports the suitability of our analysis.

In conclusion, we have proposed a general framework for the decompression dynamics of polymers. Aside from a basic equation of the nonlinear diffusion type, uniform approximation has been shown to be useful. We applied the idea and method to the problems of polymer expansion, unfolding and the ejection. We believe that, for the ejection problem in particular, this provides the first-ever consistent description with both the driving force and the dissipation mechanism clearly identified.

We would like to end with some remarks and perspectives; (I) One may wonder how the ejection process of a polymer from a planar slit numerically studied in [13, 26] is described. We point out the softness of the two-dimensionally confined polymer, i.e., its elastic modulus $\sim (k_BT)/R_0^3$ is small compared to the driving osmotic force $\sim (k_BT)/R_0$, where $R_0 \approx 0.5$ and $R_0$ are the lateral size of the confined chain and the slit distance. In contrast, in the ejection process from a closed cavity, both the elastic modulus and the driving force are dictated by the mesh size $\xi$. In the former case, the entire chain cannot respond to the ejection force acting on a particular monomer residing at the pore immediately, and the highly nonequilibrium process of the front evolution associated with the tension propagation along the chain would occur [21], while in the latter, the pressure drop is transmitted not along the chain, but radially from the pore. These differences in the underlying physics are indeed a consequence of the different confinement regimes [13, 14]. (II) The current description based on the analogy with the semidilute solution cannot be applied to the very dense system with $\phi \approx 1$. In such a densely compressed situation, one has to deal with solvent diffusion and permeation into the globular chain along with the decompression. In addition, a self-entanglement may be formed for a very long chain, which alters the dynamics qualitatively [5, 23, 24]. (III) We have assumed that the polymer is intrinsically flexible. As discussed in ref. [14], the effect of the chain stiffness would have a pronounced effect in a confined space, which alters the scaling structure of the free energy. We hope that these points would be clarified in future studies.

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[27] \( \tau_0 \) depending on details of simulations is used merely for making the proportional factor one. We have used \( \tau_0 = 7.2 \) Monte Carlo steps for [18] and \( \tau_0 = 26.4 \) for [17].

[28] The value is modified as \( m = 1/(3\nu - 1) \) without hydrodynamics since the transport coefficient is \( L \approx 1/(qa) \).