

Rouse vs. Zimm Regime: Hydrodynamic Interactions

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The Rouse and the Zimm regime are two different scaling regimes in polymer dynamics. While the Rouse regime neglects hydrodynamic interactions the Zimm regime takes these into account. Before we can dive into the details of the differences we need to work through some more fundamental stuff. Starting off with the fundamental equation of hydrodynamics we move on to hydrodynamic interactions. Then some basics of polymer physics are discussed such that we can understand the scalings in the two regimes.

I. HYDRODYNAMIC INTERACTIONS

There are several approaches for the description of fluids in physics. The Navier-Stokes equation is a continuum approach to describe fluid dynamics. The Navier-Stokes equation can either be derived from the Boltzmann transport equation or motivated from the conservation of mass and momentum in 3D. We will approach the latter. The nonlinearity makes it hard to solve and the proof of existence of a strong solution to the Navier-Stokes equation is a Millenium Problem in mathematics. The fluid is characterised by its flow field $\mathbf{u}(\mathbf{r}, t)$. One can plug in an arbitrary \mathbf{r} and t to obtain the velocity of the volume element at those values¹.

The continuity equation is the mathematical form of mass conservation. The change of the density is proportional to the change of the flux (momentum density), e.g. if a certain amount of fluid is removed from the considered volume via a pipe, then the decrease of the fluid mass is proportional to the flux through that pipe. The continuity equation is just the differential formulation of that example. The standard continuity equation reads

$$\partial_t \rho + \nabla \cdot \mathbf{u} = 0. \quad (1)$$

Because liquids are in general incompressible we assume a constant density $\rho(\mathbf{r}, t) = \rho$. Thus all derivatives of the density vanish and the continuity equation changes to

$$\nabla \cdot \mathbf{u} = 0. \quad (2)$$

Newton's second law states that if a force is exerted onto an object its momentum changes, i.e. $\mathbf{F} = \dot{\mathbf{p}}$. The momentum \mathbf{p} is equal to $m\mathbf{u}$. We divide Newton's second law by the volume to obtain all quantities as densities. The force acting on a bulk of fluid can be split into internal forces and external forces¹. The internal forces are given by the divergence of the stress tensor, cf. figure 1.

$$\frac{d}{dt}(\rho\mathbf{u}) = \mathbf{f}_{\text{int}} + \mathbf{f}_{\text{ext}} = \nabla \cdot \hat{\boldsymbol{\sigma}} + \mathbf{f}_{\text{ext}} \quad (3)$$

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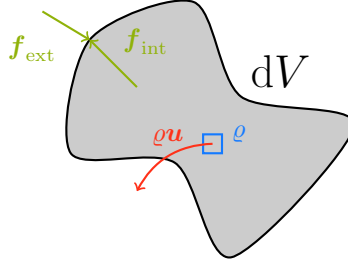


FIG. 1. For the derivation of Navier-Stokes we consider an infinitesimal volume element dV .

Now we carry out the derivative on the left hand side. Because it is a total derivative we need to take care of the arguments of $\mathbf{u}(\mathbf{r}, t)$ as well.

$$\varrho \frac{d}{dt} \mathbf{u}(\mathbf{r}, t) = \varrho \left(\frac{\partial \mathbf{u}}{\partial t} + \frac{\partial \mathbf{u}}{\partial \mathbf{r}} \frac{\partial \mathbf{r}}{\partial t} \right) = \varrho \left(\frac{\partial \mathbf{u}}{\partial t} + (\mathbf{u} \cdot \nabla) \mathbf{u} \right). \quad (4)$$

Plugging this into Newton's second law leaves us with a preliminary form of the Navier-Stokes equation.

$$\varrho \left(\frac{\partial}{\partial t} + \mathbf{u} \cdot \nabla \right) \mathbf{u} = \nabla \cdot \hat{\boldsymbol{\sigma}} + \mathbf{f}_{\text{ext}}. \quad (5)$$

From continuum mechanics one can derive the linear stress constitutive equation

$$\hat{\boldsymbol{\sigma}} = -p\mathbb{1} + \eta [\nabla \mathbf{u} + (\nabla \mathbf{u})^T]. \quad (6)$$

The stress inside dV always incorporates the pressure. For fluids an additional term is present, the Jacobian of the flow field with the scale factor η which is called viscosity. The Jacobian transports the momentum along the shear direction¹. The transposed Jacobian is needed to ensure the symmetry of $\hat{\boldsymbol{\sigma}}$. Plugging this in, we find the Navier-Stokes equation for an incompressible and isotropic Newtonian fluid

$$\varrho \left(\frac{\partial}{\partial t} + \mathbf{u} \cdot \nabla \right) \mathbf{u} = -\nabla p + \eta \nabla^2 \mathbf{u} + \mathbf{f}_{\text{ext}} \quad (7)$$

The units of the Navier-Stokes equation can be rescaled such that all constants are unified in one, the so called Reynolds number. The Reynolds number is the quotient of inertial forces LU and viscous forces ν .

$$\begin{aligned} \nu &= \frac{\eta}{\varrho}, \quad \mathbf{u}' = \frac{\mathbf{u}}{U}, \quad p' = \frac{p}{\varrho U}, \quad \mathbf{f}'_{\text{ext}} = \frac{\mathbf{f}_{\text{ext}} L}{U}, \\ \frac{\partial}{\partial t'} &= \frac{L}{U} \frac{\partial}{\partial t}, \quad \nabla' = L \nabla \\ \left(\frac{\partial}{\partial t'} + \mathbf{u}' \cdot \nabla' \right) \mathbf{u}' &= -\nabla' p' + \underbrace{\frac{\nu}{LU}}_{1/\text{Re}} \nabla'^2 \mathbf{u}' + \mathbf{f}'_{\text{ext}} \end{aligned} \quad (8)$$

The two quantities L and U are called characteristic length and speed. One can estimate the Reynolds numbers by plugging in characteristic length and speed. For a human

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swimming in water one chooses for example $L = 1$ m, because the height of a human is measured in metres and $U = 1$ m s⁻¹, because that is about the speed at that a human moves in water.

For water ($\rho = 10^3$ kg m⁻³ and $\eta = 10^{-3}$ N s m⁻²) the typical regime of Reynolds numbers in everyday life ($L = 1$ m and $U = 1$ m s⁻¹) is of the order of $Re \approx 10^6$. This does not hold for polymers, because their spacial extent is only of the order of a few nano- to micrometres. Assuming $L = 10^{-6}$ m and $U = 10^{-6}$ m s⁻¹ we eventually find $Re \approx 10^{-6}$.

With such a low Reynolds number the left hand side of the Navier-Stokes equation (7) can be neglected and we are left with

$$\eta \nabla^2 \mathbf{u} - \nabla p + \mathbf{f}_{\text{ext}} = 0 \quad (9)$$

which is called the Stokes equation or creeping flow equation¹. Because this equation does no longer ensure continuity we need to extend it to a set of two equations, where the second one is the continuity equation for constant density

$$\nabla \cdot \mathbf{u} = 0. \quad (10)$$

The pressure of the fluid can be calculated in a self consistent way and does not depend on the flow field anymore. Therefore take the divergence of the Stokes equation to obtain

$$\nabla^2 p = \nabla \cdot \mathbf{f}_{\text{ext}}. \quad (11)$$

The vorticity is defined as $\boldsymbol{\Omega} = \nabla \times \mathbf{u}$ and propagates the hydrodynamic interactions². Taking the curl of the Navier-Stokes equation and plugging in the vorticity one obtains a differential equation for the vorticity which is of diffusion type.

$$\frac{\partial}{\partial t} \boldsymbol{\Omega} = \nu \nabla^2 \boldsymbol{\Omega}. \quad (12)$$

The relaxation time of this diffusion is $\tau = L^2/\nu$. For short length scales as for micro organisms $L \approx 10^{-6}$ m this relaxation is of the order of $\tau \approx 10^{-6}$ s and is therefore assumed to be instantaneous, i.e. no delay effects are taken into account.

If particles are dissolved in the fluid they interact via their respective flow field. One can think of these interactions as particles pushing and pulling each others with their stern and bow waves (unless that on tiny length scales there is no such thing as waves). Through the flow field a particle induces forces and torques which are exerted on other particles. This coupling is scaled by the elements of the mobility tensor $\hat{\boldsymbol{\mu}}$

$$\mathbf{v}_i = \sum_j (\hat{\boldsymbol{\mu}}_{ij}^{\text{tt}} \mathbf{F}_j + \hat{\boldsymbol{\mu}}_{ij}^{\text{tr}} \mathbf{M}_j) \quad (13)$$

$$\boldsymbol{\omega}_i = \sum_j (\hat{\boldsymbol{\mu}}_{ij}^{\text{rt}} \mathbf{F}_j + \hat{\boldsymbol{\mu}}_{ij}^{\text{rr}} \mathbf{M}_j) \quad (14)$$

where

$$\hat{\boldsymbol{\mu}} = \begin{bmatrix} \hat{\boldsymbol{\mu}}^{\text{tt}} & \hat{\boldsymbol{\mu}}^{\text{tr}} \\ \hat{\boldsymbol{\mu}}^{\text{rt}} & \hat{\boldsymbol{\mu}}^{\text{rr}} \end{bmatrix} \quad (15)$$

which is positive definite and symmetric². The indices “tt” and “rr” denote the translational and rotational modes, respectively and “tr” and “rt” their coupling. For the further discussion only the translational component is relevant.

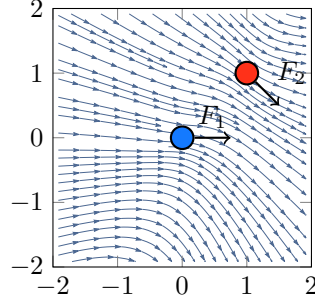


FIG. 2. Two particles exerting a force on the fluid indicated by the arrows. The complete flow field is a superposition of the two single particle fields².

In the Stokes equation one has the Laplacian of the flow field. For this type of differential equation one can determine Green's function. The fluid flow and the pressure are proportional to the external force. Transforming the Stokes equation to Fourier space yields³

$$\mathbf{u}(\mathbf{k}) = \hat{\mathbf{T}}(\mathbf{k}) \cdot \mathbf{f}_{\text{ext}}. \quad (16)$$

The tensor $\hat{\mathbf{T}}(\mathbf{k})$ is called Oseen matrix and reads

$$\hat{\mathbf{T}}(\mathbf{k}) = \frac{1}{\eta k^2} \left[\mathbb{1} + \frac{\mathbf{k}\mathbf{k}}{k^2} \right] \quad (17)$$

or in real space

$$\hat{\mathbf{T}}(\mathbf{r}) = \frac{1}{8\pi\eta} \frac{1}{r} \left[\mathbb{1} + \frac{\mathbf{r}\mathbf{r}}{r^2} \right]. \quad (18)$$

The linearity of Stokes equation allows for the superposition of the flow fields, i.e.

$$\mathbf{u}(\mathbf{r}) = \sum_i \int d\mathbf{r}_i \hat{\mathbf{T}}(\mathbf{r} - \mathbf{r}_i) \cdot \mathbf{f}_{\text{ext}}^{(i)}. \quad (19)$$

As an example one can find in figure 2 the joint flow field of two particles which exert forces onto the fluid.

Up to now the description of hydrodynamic interactions was confined to the action of one particle onto another. But if particle one influences the position of particle two the distancing of particle two will result in a change of its flow field and thus induces a backaction on particle one. This ping-pong game of interactions continues in principle forever, though the interaction decays faster for higher orders. To account for the backaction the distance between the particles one and two is expanded into powers and after three iterations (i.e. action and backaction onto oneself) one has the interaction matrix

$$\hat{\mathbf{M}}(\mathbf{r}) = \frac{3}{4} \frac{a}{r} \left[\mathbb{1} + \frac{\mathbf{r}\mathbf{r}}{r^2} \right] + \frac{1}{2} \frac{a^3}{r^3} \left[\mathbb{1} - 3 \frac{\mathbf{r}\mathbf{r}}{r^2} \right]. \quad (20)$$

With this the mobility tensor can be constructed akin to the Oseen matrix, which is now called the Rotne-Prager approximation⁴

$$\begin{aligned} \hat{\boldsymbol{\mu}}_{ii}^{\text{tt}} &= \frac{1}{6\pi\eta a} \mathbb{1}, \\ \hat{\boldsymbol{\mu}}_{ij}^{\text{tt}} &= \left(1 + \frac{1}{6} a^2 \nabla_j \right) \hat{\mathbf{M}}(\mathbf{r}_i - \mathbf{r}_j), \quad i \neq j. \end{aligned} \quad (21)$$

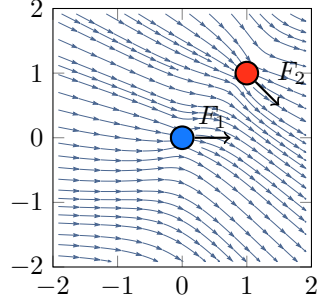


FIG. 3. As in figure 2 two particles exert a force on the fluid indicated by the arrows. This time the Rotne-Prager approximation has been calculated. One can see that in the near field (between the particles) the flow field has a considerably different shape than for the Oseen matrix calculation, whereas the far field stays nearly invariant².

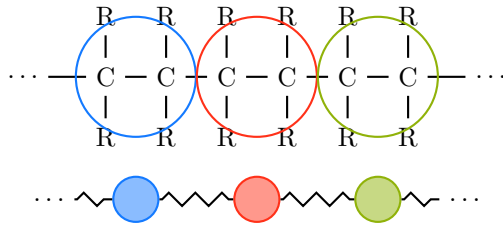


FIG. 4. A polymer is coarse-grained by neglecting irrelevant microscopic properties. Here the monomers are replaced by beads and the bonds connecting the monomers by springs.

In addition to the r^{-3} term, which scales like the Oseen matrix, one now also has the r^{-5} term. It is obvious that this term will become large for small distances, i.e. the near field will substantially differ in comparison to the flow field as calculated with the Oseen matrix, cf. figure 3.

II. ROUSE REGIME

Before we can start discussing the details of the Rouse regime we need to familiarise with a couple of terms in polymer physics.

Polymers are built by monomers connected with bonds. For simplicity these monomers can be replaced by “beads”. Since we are not interested in the quantum mechanics of the bond we can model it as a spring, cf. figure 4. Significant observables of a polymer are the centre of mass

$$\mathbf{R} = \frac{1}{N} \sum_{i=1}^N \mathbf{R}_i, \quad (22)$$

the radius of gyration (a measure for the spacial extent of a polymer)

$$R_g^2 = \frac{1}{2N^2} \sum_{i=1}^N \langle (\mathbf{R}_i - \mathbf{R})^2 \rangle, \quad (23)$$

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and the end to end distance (a measure for the length of a polymer)

$$R_e^2 = (\mathbf{R}_N - \mathbf{R}_1)^2. \quad (24)$$

For the radius of gyration and the end to end distance one finds the scaling behaviour $\langle R_e^2 \rangle \propto \langle R_g^2 \rangle \propto N^{2\nu}$ with the Flory exponent ν^5 .

The dynamics of a polymer at zero temperature would be quite boring as nothing moves. For finite temperature we have to take into account thermal fluctuations in the surroundings regarded to a Brownian motion. For Brownian motion we assume an equation of motion with a damping term with the friction coefficient ζ and a Gaussian distributed random force $\mathbf{f}(t)$. This leads to the Langevin equation

$$m \frac{d^2 \mathbf{x}}{dt^2} = -\zeta \frac{d\mathbf{x}}{dt} + \mathbf{F}(x, t) + \mathbf{f}(t). \quad (25)$$

The transition to Brownian dynamics follows if we let $m \rightarrow 0$ and assume a conservative force which can thus be written as the gradient of a potential⁵.

$$-\zeta \frac{d\mathbf{x}}{dt} - \nabla U + \mathbf{f}(t) = 0. \quad (26)$$

It is important that $\langle f_\alpha(t) \rangle = 0$ and $\langle f_\alpha(t) f_\beta(t') \rangle = 2\zeta k_B T \delta(t - t') \delta_{\alpha\beta}$ for Brownian motion to take place. The generalised Langevin equation can be derived from the Focker-Planck equation (Focker-Planck describes the time evolution of the probability density for stochastic variabls)⁵. Instead of the friction on the left hand side we now have coupling matrices. The generalised Langevin equation reads

$$\frac{d}{dt} \mathbf{x}_n = \sum_m \hat{\mathbf{L}}_{nm} \left(-\frac{\partial U}{\partial x_m} + \mathbf{f}_m(t) \right) + \frac{k_B T}{2} \sum_m \frac{\partial}{\partial x_m} \hat{\mathbf{L}}_{nm} \quad (27)$$

with the coupling matrices $\hat{\mathbf{L}}_{nm}$.

For the Rouse regime we assume a polymer with N beads, where each bead has the same friction ζ with the surroundings. In contrast to the Zimm regime, which will be discussed later, we neglect for now any hydrodynamic interactions between the beads⁵. The equation of motion as in (26) now reads

$$\zeta \frac{d\mathbf{R}_n}{dt} = -k(2\mathbf{R}_n - \mathbf{R}_{n+1} - \mathbf{R}_{n-1}) + \mathbf{f}_n \quad (28)$$

with the discretised derivative of the spring potential. This equation has the form of N coupled oscillators. To decouple these equations we introduce the normal coordinates⁵

$$\mathbf{X}_p = \frac{1}{N} \sum_{n=1}^N \mathbf{R}_n(t) \cos\left(\frac{p\pi n}{N}\right), \quad p = 0, 1, 2, \dots \quad (29)$$

Plugging these into the equation of motion one has

$$\zeta_p \frac{\partial}{\partial t} \mathbf{X}_p = -k_p \mathbf{X}_p + \mathbf{f}_p \quad (30)$$

with rescaled frictions, couplings, and forces. The motion of the polymer has been decomposed into independent modes, the Rouse modes, each of which is capable of

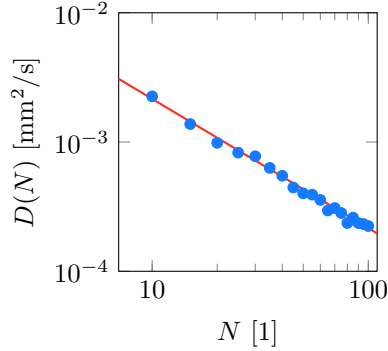


FIG. 5. Numerical simulation of a polymer with $N = 10$ to 100 beads in Langevin dynamics. The fitted slope scales with $1/N$ and coincides with the data quite well.

independent motion⁶. The correlation function of the normal coordinates can be calculated and shows an exponential decay with the relaxation time τ_p of the Rouse modes.

$$\langle \mathbf{X}_{p\alpha}(t) \mathbf{X}_{q\beta}(0) \rangle = \delta_{pq} \delta_{\alpha\beta} \frac{k_B T}{k_p} e^{-t/\tau_p}, \quad \tau_p = \frac{\zeta N^2 b^2}{3\pi^2 p^2 k_B T} \quad (31)$$

The relaxation time τ_p is proportional to the Rouse time $\tau = p^2 \tau_p$ which is independent of the mode p . One can express the original coordinates in terms of the normal coordinates

$$\mathbf{R}_n = \mathbf{X}_0 + 2 \sum_{p=1}^{\infty} \mathbf{X}_p \cos\left(\frac{p\pi n}{N}\right). \quad (32)$$

It is obvious that the zeroth mode \mathbf{X}_0 corresponds to motion of the centre of mass coordinate.

$$\mathbf{R} = \frac{1}{N} \sum_{i=1}^N \mathbf{R}_i = \mathbf{X}_0 \quad (33)$$

Because we know the correlation of the normal coordinates we can derive an expression for the mean square displacement of the centre of mass of the polymer.

$$\langle (\mathbf{R}(t) - \mathbf{R}(0))^2 \rangle = \sum_{\alpha=x,y,z} \langle (\mathbf{X}_{0\alpha}(t) - \mathbf{X}_{0\alpha}(0))^2 \rangle = 6 \frac{k_B T}{N\zeta} t. \quad (34)$$

From the mean square displacement we can compute the diffusion coefficient via the Einstein relation.

$$D = \lim_{t \rightarrow \infty} \frac{1}{6t} \langle (\mathbf{R}(t) - \mathbf{R}(0))^2 \rangle = \frac{k_B T}{N\zeta} \quad (35)$$

A numerical simulation verifies this result, cf. figure 5.

III. ZIMM REGIME

The Zimm regime is an extension to the Rouse regime. We consider the same setup as for the Rouse regime above, i.e. a coarse-grained polymer with N beads, but this time we take into account hydrodynamic interactions. The hydrodynamic coupling

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between the beads is now described by coupling matrices. We choose the Oseen matrix for interactions between different beads and the unity matrix for the interaction of a bead with itself⁵.

$$\hat{\mathbf{H}}_{nn} = \frac{1}{\zeta} \mathbb{1} \quad (36)$$

$$\begin{aligned} \hat{\mathbf{H}}_{nm} &= \hat{\mathbf{T}}(\mathbf{r}_{nm}), \quad n \neq m \\ &= \frac{1}{8\pi\eta} \frac{1}{r_{nm}} \left[\mathbb{1} + \frac{\mathbf{r}_{nm}\mathbf{r}_{nm}}{r^2} \right] \end{aligned} \quad (37)$$

with $\mathbf{r}_{nm} = \mathbf{R}_n - \mathbf{R}_m$. Because the coupling matrices only depend on the distance and not on the position of the particles the second term in the generalised Langevin equation (27) drops out and we are left with

$$\frac{d\mathbf{R}_n}{dt} = \sum_m \hat{\mathbf{H}}_{nm} \cdot \left(-\frac{\partial U}{\partial \mathbf{R}_m} + \mathbf{f}_m(t) \right) \quad (38)$$

Because tensor equations are not easily tractable Zimm introduced a simplification⁷. He replaced the Oseen matrix by its equilibrium average. It can be shown that the result only depends on the “index distance” between the beads.

$$\begin{aligned} \hat{\mathbf{H}}_{nm} &\rightarrow \langle \hat{\mathbf{H}}_{nm} \rangle_{\text{eq}} = \int d\{\mathbf{R}_n\} \hat{\mathbf{H}}_{nm} f_{\text{eq}}(\{\mathbf{R}_n\}, t) \\ &= \frac{1}{(6\pi^3 |n-m|)^{1/2} \eta b} \mathbb{1} \\ &\equiv h(n-m) \mathbb{1}. \end{aligned} \quad (39)$$

Therefore the Langevin equation becomes linear again.

$$\frac{\partial}{\partial t} \mathbf{R}_n(t) = \sum_m h(n-m) \left(k \frac{\partial^2}{\partial m^2} \mathbf{R}_m(t) + \mathbf{f}_m(t) \right) \quad (40)$$

It is again possible to find normal coordinates but this time the calculation is much more sophisticated⁵. In principle the steps are the same as for the Rouse regime. One finds that the diffusion coefficient is proportional to $N^{-\nu}$.

$$D = \frac{k_B T}{\eta N^\nu b} \propto \frac{1}{N^\nu} \quad (41)$$

The exponent ν is called Flory exponent. There are different values for the Flory exponent. For a polymer without excluded volume effects one finds $\nu = 1/2$. For the Flory mean field it was found $\nu = 0.6$ and renormalisation group calculations obtained $\nu \approx 0.588$. For a polymer with excluded volume in a lattice-Boltzmann fluid, numerical data is presented in figure 6.

IV. ROUSE VS. ZIMM

In the Rouse regime we studied a coarse-grained polymer under Langevin dynamics, which does not incorporate hydrodynamic interactions. It was found that the diffusion

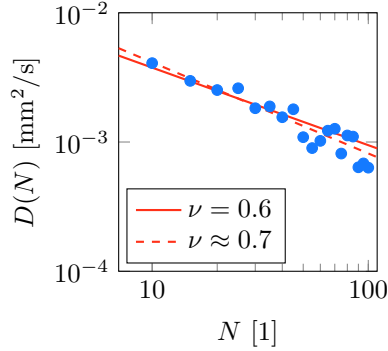


FIG. 6. Numerical simulation of a polymer with $N = 10$ to 100 beads in a lattice-Boltzmann fluid with explicit excluded volume interactions. Two functions were fitted, the solid line is proportional to $1/N^{0.6}$, whereas for the dashed line the exponent was also determined by the fitting routine.

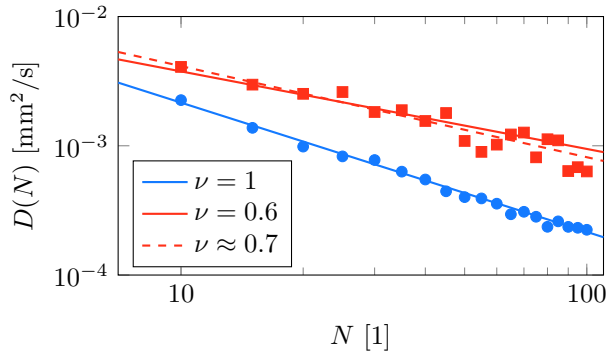


FIG. 7. Comparison of the different scalings for the Rouse and the Zimm regime. Here it is obvious to see that they obey different power laws.

coefficient scales with $D \propto 1/N$. For the Zimm regime, in contrast, we took into account hydrodynamic interactions by means of the Oseen matrix. Here the diffusion coefficient scales with $D \propto 1/N^\nu$, where $\nu < 1$ depends on the boundary conditions. Figure 7 gives a visual comparison of the two.

Hydrodynamic interactions might be screened by different circumstances. If a polyelectrolyte (charged polymer) is dissolved in an ionic liquid, a cloud of counter ions forms around it. When an electric field is applied the polyelectrolyte and the oppositely charged ions move in rivalling directions which erase each other effectively by a zero net momentum transfer. This results in a screening of hydrodynamic interactions between the monomers. The polyelectrolyte behaves like a string of N inert spheres. The diffusion coefficient is then again given by the Rouse diffusion³.

Polymers may also be immersed in dense polymeric solutions (i.e. a polymer dissolved mainly in polymers). The polymers in the solvent change the local viscosity of the bare solvent and lead to a faster exponential decay of the hydrodynamic interactions³. One can say that the Zimm regime merges into the Rouse regime in absence of hydrodynamic interactions.

In the previous text it was emphasised that the different regimes exhibit different

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scaling, i.e. we could detect the regimes by their scaling behaviour. To this end we take into account several correlation functions^{8,9}. The correlation function $g_1(t)$ describes the mean-square displacement of a monomer i (usually the central monomer).

$$g_1(t) = \langle (\mathbf{R}_i(t) - \mathbf{R}_i(t_0))^2 \rangle \propto t^{2/z}. \quad (42)$$

For $\tau_b \ll t \ll \tau$, where τ_b is the time of the ballistic regime and τ is the Rouse and the Zimm time, respectively, the exponent z scales according to the regime, viz. $z = 2 + 1/\nu$ for Rouse and $z = 3$ for Zimm. The correlation function $g_2(t)$ quantifies the mean-square displacement of a monomer i from the centre of mass (again, usually for the central monomer).

$$g_2(t) = \langle [(\mathbf{R}_i(t) - \mathbf{R}(t)) - (\mathbf{R}_i(t_0) - \mathbf{R}(t_0))]^2 \rangle \quad (43)$$

As above, for $\tau_b \ll t$ it scales like t^0 and one can extract therefore the Rouse and the Zimm time. For Rouse one has $\tau \propto N^2$ and for Zimm one has $\tau \propto N^{3\nu}$. The correlation function $g_3(t)$ has already been present in the calculation of the diffusion coefficient but will be repeated for the sake of completeness. It is the mean-square displacement of the centre of mass.

$$g_3(t) = \langle (\mathbf{R}(t) - \mathbf{R}(t_0))^2 \rangle = 6Dt \quad (44)$$

For the diffusion coefficient one finds for $\tau_b \ll t$, that $D \propto 1/N$ for the Rouse regime and $D \propto 1/N^\nu$ for the Zimm regime.

Another measure for the regime is the dynamic structure factor

$$S(k, t) = \frac{1}{N} \sum_{i,j} \langle e^{i\mathbf{k}(\mathbf{R}_i(t) - \mathbf{R}_j(t_0))} \rangle \propto S(k, 0) f(k^z t) \quad (45)$$

where z is defined as for $g_1(t)$.

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