

Dynamics of Polymeric Fluids in Transient-State Theory

JUNHUA WU

Max-Planck-Institute for Polymer Research, P.O. Box 3148, 55021 Mainz, Germany* and Anhui Provincial Engineering Consulting Institute, 100 Lujiang Road, Hefei, 230061 Anhui, P.R. China

SYNOPSIS

Transient-state theory recently proposed has enabled us to describe the chain length dependence of viscosity of polymeric melts from the Rouse to entangling regimes by the single equation which also takes the factor of temperature into account. On the basis of this theory, this contribution attempts to treat the effect of temperature on viscosity and provides a molecular explanation to the coefficients of M -dependence in the WLF equation, obtaining the activation energy ΔE_0 and elastic interaction parameter a for example selected. A reinterpretation from a molecular viewpoint directly leads to the common observation of the M -dependence of the glass transition temperature. The mathematical expressions are developed for diffusion coefficient D_s , showing the scaling behavior for special cases as M^{-1} and $M^{-2.4}$ below and above the entanglement coupling mass M_e , respectively. Any deviation from the scaling can be accounted by the quantum confinement effect a . The terminal relaxation time τ_D behaves in the same way as η above the onset of entanglement. It is found that both D_s and τ_D scale on temperature in the way analogous to the WLF correlation. In addition, an expression for Young's modulus is presented by a molecular deduction. The predictions are in consistence with existing experimental data via the adjustment of a which can correlate more findings difficult to be accommodated into conventional theories.

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INTRODUCTION

We have initiated a new approach to handle the transport problem of glass-forming polymeric fluids in the framework of molecular physics by considering that the transportation property of a chain is determined by two competent factors, i.e., the spectrum of phonons or conformons of the chain itself and its interaction with the neighboring medium or so-called "effect of quantum constraints."¹ The effect of the molecular weight M and temperature T enters naturally into the master equations for viscosity and diffusivity as a whole. The expression of diffusivity $D_c(M, T)$ for a whole chain derived in the precedent work is given by

$$D_c(M, T) = A \exp(-\Delta E_0/k_B T) \times \exp\left(\frac{1}{2} \hbar \frac{a}{\sqrt{M}} / k_B T\right) \times \frac{1}{2\pi^2 c_s^3} \left(\frac{k_B T M_c}{M \hbar}\right)^3 \times \int_0^{M\theta_c/M_c T} \frac{x^2}{\exp(x) - 1} dx, \quad (1)$$

where A is a proportionality, $\theta_c = \hbar \omega_c / k_B$, ω_c is the upper limit of the phonon angular frequency, k_B is Boltzmann's constant, ΔE_0 is the activation energy, \hbar is the Planck constant divided by 2π , T is the temperature, c_s is the velocity of sound, M is the molecular weight, M_c is the characteristic molecular weight of a segment relevant to phonons or the entangling molecular weight of a transient network, a is an important parameter related to the elasticity of the chain. It is worthwhile to emphasize that the diffusivity $D_c(M, T)$ describe the mobility of the whole chain and it should be made different from that of a subchain, in general.

* To whom correspondence should be addressed at Max-Planck-Institute for Polymer Research, P.O. Box 31248, 55021 Mainz, Germany.

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Correspondingly we have the master equation for viscosity of glass forming polymers

$$\eta(M, T) = C_0 T^{-2} M^3 \exp(\Delta E_0/k_B T) \times \exp\left(-\frac{1}{2} \hbar \frac{a}{\sqrt{M}} / k_B T\right) \times \left\{ \int_0^{M\theta_c/M_c T} \frac{x^2}{\exp(x) - 1} dx \right\}^{-1}. \quad (2)$$

Here $C_0 = 2\pi^2 K_0 c_s^3 \hbar^3 / A k_B^2 M_c^3$, K_0 is a structural factor, usually taken independent of M and T . For a large term of

$$\frac{M\theta_c}{M_c T},$$

eq. (2) can be written as

$$\eta(M, T) = C_{00}^* T^{-2} M^3 \exp(\Delta E_0/k_B T) \times \exp\left(-\frac{1}{2} \hbar \frac{a}{\sqrt{M}} / k_B T\right) \quad (3)$$

where $C_{00}^* = 0.4160C_0$ and the product of $M_c T/\theta_c$ defines the entangled molecular weight M_e^1 .

The theoretical analysis and experimental fitting show convincingly the soundness of our reasoning over the whole range of the molecular weight including the Rouse and entangled regimes. In particular, the typical experimental data selected are well interpreted for the first time by the single master equation obtained, i.e., eq. (2). Moreover, the well-known 3.4-power law was found valid for a broad but limited spectrum of M . In this communication we revisit the classic WLF equation^{2,12,13} in a new context and touch the problems like diffusion coefficient^{3,4,12} and terminal relaxation time^{3,4,12} based on this new picture. An expression for Young's modulus of rubber elasticity⁵ is also reached by an appropriate reasoning without invoking the affine assumption. Case study is carried out to show primary applicability of the new model to experiments.

The WLF Equation Revisited

The excitation of the motion of a polymeric chain shows a strong dependence on temperature. Below a certain temperature the bosons, conformons, are frozen-in and a displacive motion of the chain is forbidden. Their "absolute zero temperature" shifts

upward to a new value T_g . Thus we may substitute T in the equation (3) by $T - T_g$ and are led to

$$\eta(M, T, T_g) = C_{00} (T - T_g)^{-2} \times \exp\left[\left(\Delta E_0 - \frac{1}{2} \hbar \frac{a}{\sqrt{M}}\right) / k_B (T - T_g)\right]. \quad (4)$$

$C_{00} = C_{00}^* M^3$. In the following derivation, only the temperature in the equation is viewed as variable and the molecular weight M treated as parameter. Choosing a reference temperature T_0 , the temperature shifting factor a_T reads

$$\log a_T = \log[\eta(M, T, T_g)/\eta(M, T_0, T_g)] \quad (5a) \\ = 2 \log \frac{T_0 - T_g}{T - T_g} + \frac{1}{2.303 k_B} \left(\Delta E_0 - \frac{1}{2} \hbar \frac{a}{\sqrt{M}} \right) \\ \times \left(\frac{1}{T - T_g} - \frac{1}{T_0 - T_g} \right). \quad (5b)$$

Simultaneously, it is a general phenomenon that the viscosity of polymers as a function of T empirically obeys the WLF (Williams-Landel-Ferry) law^{2,12}

$$\log a_T = -\frac{C_1 (T - T_0)}{C_2 + (T - T_0)}, \quad (6)$$

where C_1 and C_2 are empirical constants and can be found experimentally. Comparing both eq. (5) and (6) we find

$$C_1 = \frac{1}{2.303 k_B (T_0 - T_g)} \left(\Delta E_0 - \frac{1}{2} \hbar \frac{a}{\sqrt{M}} \right) \quad (7)$$

$$C_2 = \frac{T_0 - T_g}{1 + \frac{2k_B (T_0 - T_g)}{\Delta E_0 - \frac{1}{2} \hbar \frac{a}{\sqrt{M}}}}. \quad (8)$$

In the above treatment, we have ignored the effect of the denominator in eq. (8) on the term $(T - T_0)$ in the denominator of eq. (6) for $|T - T_0| < T_0 - T_g$, usually valid for experimental investigation and expand the logarithmic term by

$$\log \frac{T_0 - T_g}{T - T_g} \approx -\frac{T - T_0}{2.303 (T - T_g)} \quad (9)$$

for $T - T_g > |T - T_0|$. In short, eq. (5) can be approximated to eq. (6) supplemented by eq. (7)

and (8) describing the constants. Therefore it may be concluded that the WLF equation is a natural result of the master equation (4) for viscosity.

***M*-Dependence of C_1 and C_2 ; Activation Barrier ΔE_0**

Now we discuss the coefficients C_1 and C_2 as a function of M because of the availability of relevant experimental data⁶ to shed more light on the essence of the dynamics in polymer melts. In the common scheme man takes the energetic barrier constant and independent of M . In our reasoning, we have proposed that there is an extra term from quantum confinement, contributing to the activation of the chain. T_g keeps constant. Then the constant C_1 in the WLF equation is, from eq. (7), subject to

$$C_1 = B \left(\Delta E_0 - \frac{1}{2} \hbar \frac{a}{\sqrt{M}} \right), \quad (10)$$

$$B = \frac{1}{2.303 k_B (T_0 - T_g)}.$$

This equation states an explicit relationship between the constant C_1 and the molecular weight M . Thus it is possible to examine the relation in more detail and get information on the activation energy ΔE_0 and elastic response a , two important parameters determining the dynamic behavior of a system. First the plotting of $C_1 \sim M^{-1/2}$ should show a linear

correlation between C_1 and $M^{-1/2}$. In fact, the experiment on poly(butadiene) selected as example verifies this prediction (refer to Figure 1). Then we get ΔE_0 and a from the slope and intercept of the linear correlation

$$B\Delta E_0 = 3.61 \quad \text{and} \quad \frac{1}{2} \hbar a B = 30.27 \quad (10a)$$

If we introduce the formal expression of B and approximate $(T_0 - T_g)$ by (298 - 175) K used in the experiment or the value of 162 K from the simulation of C_2 dependent on M (see below), it is found

$$\Delta E_0 = 8.5 \sim 11.3 \text{ kJ/mol} \quad (10b)$$

a value reasonable for a subchain to be activated to change its conformation and comparable to that of a recent measurement by NMR done on deuterated poly(butadiene) in solutions⁷ and other reports,⁸ although some subtlety should be made to differentiate the difference as a result of the experimental conditions varied.

In the previous analysis we have obtained the curves of the master equation fit to the viscosity data of poly(butadiene) reported⁶

$$\eta = 10^{-9.0} M^3 e^{-196.2/\sqrt{M}} (M > M_e);$$

$$\eta = 10^{-2.0} M e^{-23.5/\sqrt{M}} (M < M_e). \quad (10c)$$

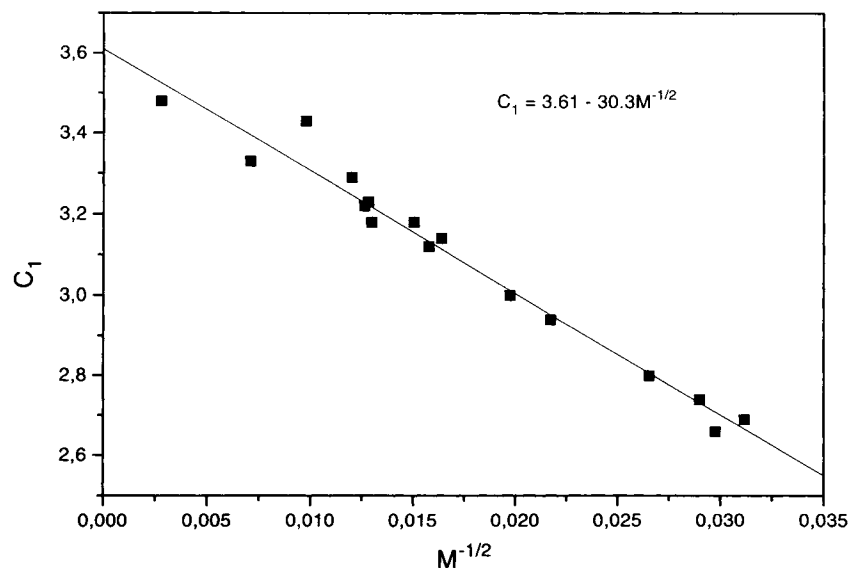


Figure 1 Molecular dependence of the coefficient C_1 in the WLF equation. The experimental data points⁶ are correlated well to eq. (10), $C_1 = 3.61 - 30.3M^{-1/2}$, giving the activation energy and interaction parameter a .

The prefactors in the natural exponents are direct related to the elastic parameter a ,

$$\frac{1}{2} \hbar a / k_B T = 196.2 (M > M_e);$$

$$\frac{1}{2} \hbar a / k_B T = 23.5 (M < M_e). \quad (10d)$$

It is not difficult to estimate that the magnitudes obtained from the analysis of both η and C_1 in light of M are of the same order for a . This kind of analysis demonstrates the self-consistence of the theory in itself and supplies information on the elastic interaction of polymers.

Experimentally substantiated, eq. (8) forecasts that C_2 increases with M . Actually, eq. (8) can be rewritten in the form

$$\frac{1}{C_2} = \frac{1}{T_0 - T_g} + \frac{1}{\frac{\Delta E_0}{2k_B} - \hbar \frac{a}{4k_B \sqrt{M}}}. \quad (8a)$$

From the plot of the measured data⁶ of C_2^{-1} against $M^{-1/2}$ as shown in Figure 2, the distribution is expectedly described by eq. (8a). The fitting produces an acceptable value of the apparent $(T_0 - T_g)$ of 162.6 K. In sum, we are able to present a (semi-) quantitative interpretation of the observed M -dependence of the constants C_1 and C_2 in the WLF equation on the molecular model proposed.

M-Dependence of T_g

In this section we reconsider the experimental observation of the M -dependence of T_g ⁵ and forward a new explanation of the activation barrier to get an expression unifying T_g and M .

Returning to the traditional scheme, it is assumed that the term of activation energy, designated as ΔE_0^* , is independent of molecular weight M . Now T_g becomes molecular-weight dependent. We call this kind of T_g an apparent glass transition temperature T_g^* and read eq. (7) in

$$C_1 = \frac{1}{2.303k_B(T_0 - T_g^*)} \Delta E_0^*. \quad (11)$$

Equating both eq. (10) and (11), the apparent glass transition temperature T_g^* dependent on M assumes the form of

$$T_g^* = T_0 - \Delta E_0^* / \left[2.303k_B B \left(\Delta E_0 - \frac{1}{2} \hbar \frac{a}{\sqrt{M}} \right) \right] \quad (12a)$$

$$T_g^* = T_0 - \frac{B_0}{1 - a_0/\sqrt{M}}, \quad (12b)$$

where $B_0 = \Delta E_0^*/[2.303k_B B \Delta E_0]$, $a_0 = \hbar a/2\Delta E_0$. When

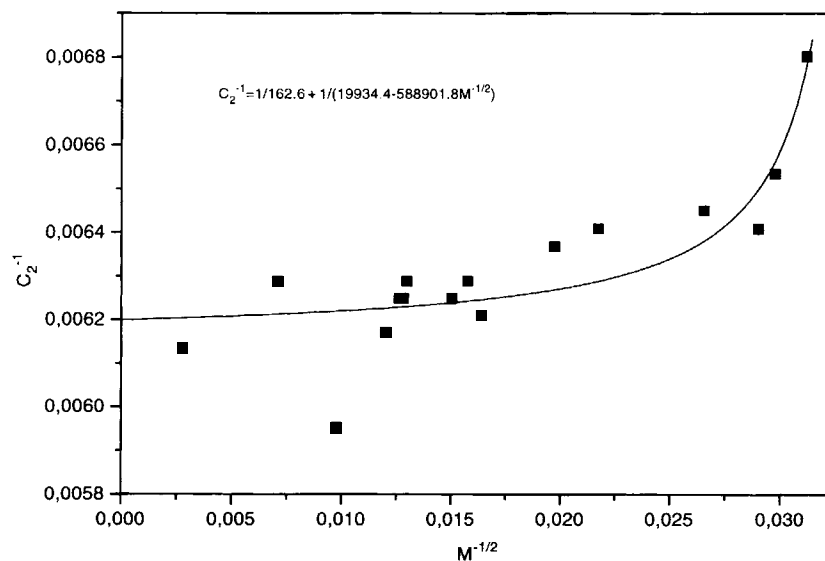


Figure 2 Molecular dependence of the coefficient C_2 in the WLF equation (data from ref. 6). The term $(T_0 - T_g)$ fit reads 162.6 K.

$$\Delta E_0 > \frac{1}{2} \hbar \frac{a}{\sqrt{M}},$$

eq. (12b) is simplified to

$$T_g^* \approx T_g^{*\infty} - \frac{B_1}{\sqrt{M}}, \quad (12c)$$

where $T_g^{*\infty} = T_0 - B_0$ as the extrapolation value at an infinite molecular weight M and $B_1 = \Delta E_0^* \hbar a / 4.606 k_B B \Delta E_0^2$. This equation is slightly different from the classic formulation⁵

$$T_g^* = T_g^{*\infty} - \frac{K}{M}. \quad (13)$$

K is a constant. The experimental data are plotted in terms of T_g via $M^{-1/2}$ and M^{-1} in Figure 3(a) and 3(b), separately. It is found that the experimental data can be correlated satisfactorily by the both equations. However, the constants in the equations show a clearer physical meaning in our case.

To sum up, the WLF scaling law is derived direct from the more fundamental principle invoked by us and its constants are quantitatively expounded. The molecular weight dependence of the glass transition temperature is interpreted as a result of quantum confining effect and their relation can be deduced from the same principle.

Diffusion Coefficient

One interesting topic in polymer physics is concerned on the diffusion coefficient of a polymeric ensemble dependent on the chain length. The coefficient is termed as D_s , purposely differentiated from D_c used before. We postulate further that experiments on diffusion measure the local mobility of a chain. This local motion involves an individual segment of a length M_c . In other words, the diffusion coefficient D_s discussed here is in general different from the cooperative diffusion coefficient D_c of a whole chain as emphasized in the previous work (refer to eq. (1) in this paper). Nonetheless they can be related to each other by an elegant equation. In the remaining part of this section, we will derive such a relation between D_s and D_c . To simplify the discussion the molecular length L is divided into two regimes, short and long, the onset of entanglement coupling acting as division line. First we consider the case of L longer than L_e (or equivalently, $M > M_e$). When a chain is under a steady shear field of a rate $\dot{\gamma}$, it experiences a force F_c (the small index

c is used as previously to emphasize the force being exerted on the whole chain) is

$$F_c = \eta \dot{\gamma}, \quad (14)$$

and so the force F_s on the subchain M_c is

$$F_s = \eta_s \dot{\gamma}. \quad (15)$$

η_s is the viscosity of the subchain. Obviously one chain of molecular weight M contains a number M/M_c of subchains of interest. Then F_c is M/M_c times larger than F_s . Thus the viscosity η_s relevant to a single segment is the times of M/M_c smaller than η and the equation below is valid,

$$\eta_s = \frac{M_c}{M} \eta. \quad (16)$$

Using the Einstein relation inversely,

$$D_s = K_0 k_B T / \eta_s \quad (17)$$

we may relate D_s to D_c and η by inserting the equations (1), (2), (16) into eq. (17),

$$D_s = \frac{M}{M_c} D_c, \quad (18)$$

and

$$D_s = \frac{M}{M_c} \frac{K_0 k_B T}{\eta}, \quad (19)$$

or

$$D_s(M, T) = A \exp(-\Delta E_0 / k_B T) \exp\left(\frac{1}{2} \hbar \frac{a}{\sqrt{M}} / k_B T\right) \times \frac{1}{2\pi^2 c_s^3} \left(\frac{k_B T}{\hbar}\right)^3 \left(\frac{M_c}{M}\right)^2 \int_0^{M\theta_c / M_c T} \frac{x^2}{\exp(x) - 1} dx. \quad (20)$$

To get an insight into the mathematical formulas just obtained, now we look at some special aspects of them. As η may be approximated by a power law

$$\eta = \eta_0 M^\alpha, \quad (21)$$

(η_0 is constant) at the high side of the molecular weight M as predicted from the analysis previously,¹ it is evident from eq. (18) that the diffusion constant D_s observes a relation

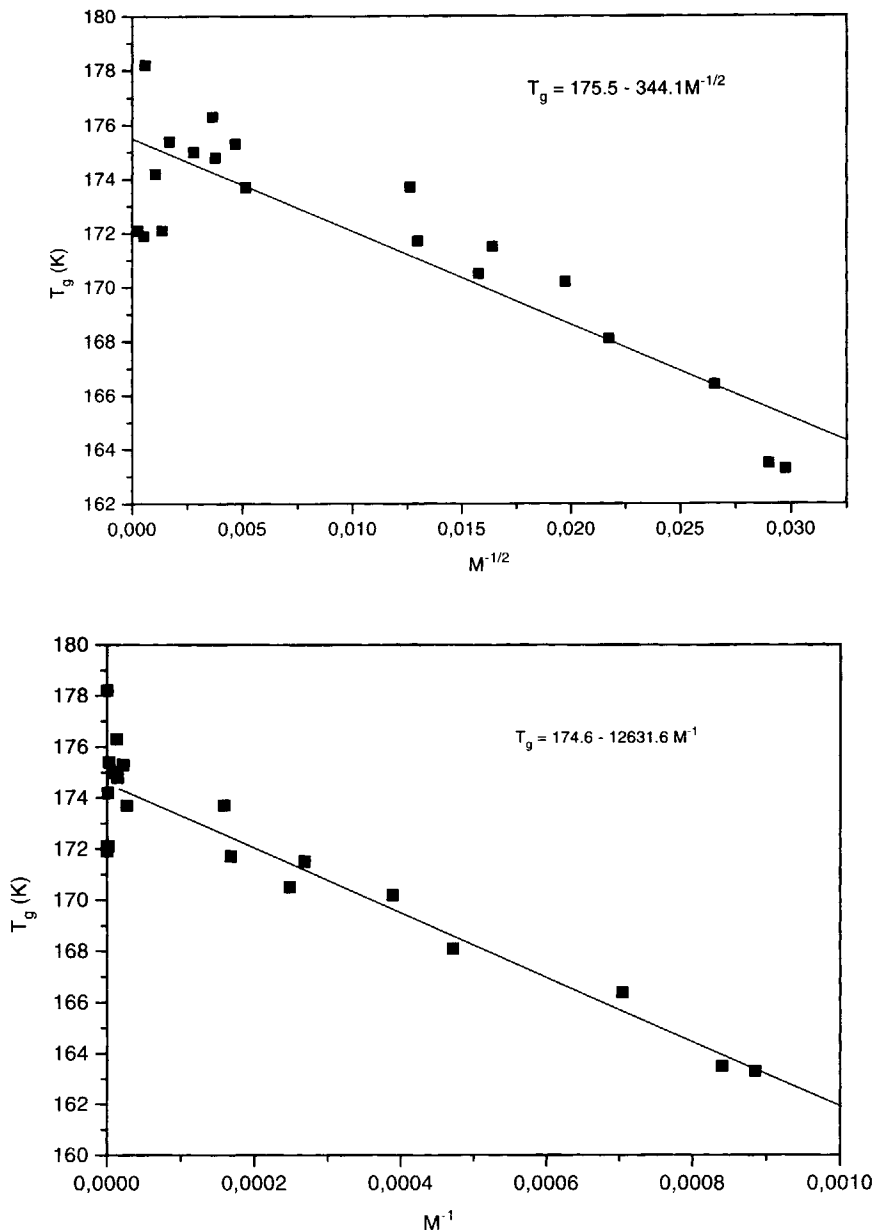


Figure 3 Molecular dependence of the glass transition temperature T_g (data from ref. 6). (a) Theoretical calculation of the present model, $T_g = 175.5 - 344.1M^{-1/2}$ (K); (b) Fitting of the classic relation, $T_g = 174.6 - 12631.6M^{-1}$ (K).

$$D_s = D_{s0}M^{-(\alpha-1)}. \quad (22)$$

D_{s0} is constant. This equation tells us that D_s follows $-(\alpha - 1)$ -power law of M as the viscosity obeys the α -power scaling. If $\alpha = 3.4$, the diffusion coefficient D_s arrives at a form

$$D_s = D_{s0}M^{-2.4}. \quad (23)$$

That is to say, the diffusion coefficient D_s decreases quickly with molecular weight M scaled by a power of -2.4 . We may also get some intuitive impression on the mobility of a chain of high molecular weight. If the prefactor D_{s0} is taken to be at the order $10^{-8} \sim 10^{-10}$ m²/s of monomeric diffusion coefficient with a mass about 100 in liquid state, the magnitude of polymeric diffusion coefficient D_s is estimated to be in the range of $10^{-10} \sim 10^{-17}$ m²/s for the molecular

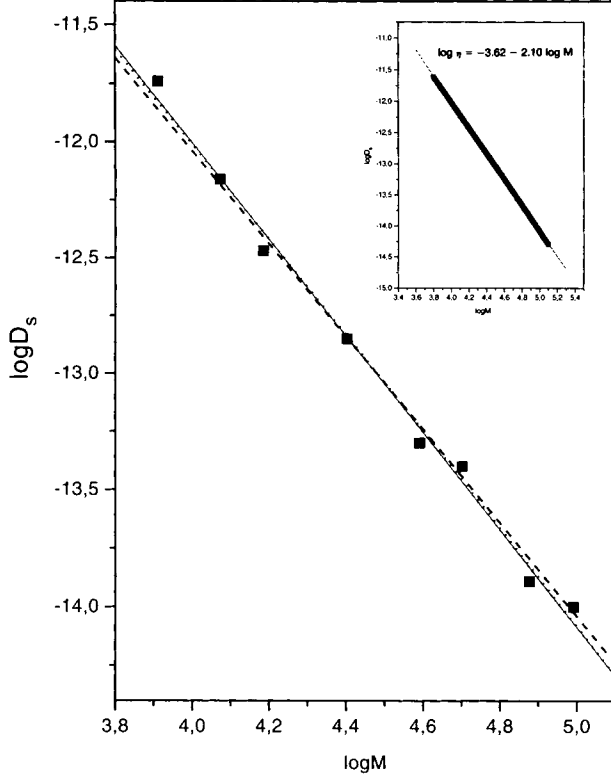


Figure 4 Molecular dependence of the diffusion constant for poly(isoprene)⁹ fit to different models. Real curve: theoretical simulation of our model, $\log \eta = -4.13 - 2 \log M + 13.32M^{-1/2}$ and the inset showing the corresponding linear regression, $\log \eta = -3.62 - 2.10 \log M$; dotted line: an apparent linear regression, $\log \eta = -3.68 - 2.08 \log M$; dashed curve: the reptation model, $\log \eta = -4.04 - 2 \log M$.

weight in the order of $10^3 \sim 10^5$. So the motion of a polymeric chain is really a very slow process.

As a primary test of the validity of eq. (20), we reanalyze the data on diffusion obtained by Fleischer and Appel.⁹ Eq. (20) is reduced to

$$D_s = D_{s0}M^{-2}\exp(a_1M^{-1/2}), \quad (20a)$$

for simplicity. Here $a_1 = \frac{1}{2}\hbar^a/k_B T$; D_{s0} and a_1 are independent of M . Figure 4 displays three types of fitting for the experimental data of poly(isoprene)⁹: result of the reptation model (scaling of M^{-2}), apparent linear regression and theoretical calculation by the present model. Generally speaking, the data points are excellently matched by all the three curves. The theoretical result of our model is almost coincident with that of the apparent linear regression and both of them seem to demonstrate a slightly better correlation. Furthermore, the data calculated from our model displays a perfect linearity (refer the inset in Figure 4) and the prefactor before the term $M^{-1/2}$ is as expected in the

same order of that obtained for poly(butadiene) as analyzed above (refer to the relevant values in eq. (10a), (10c) and (10d)), showing similar behavior in the elastic interaction of them. The exact expressions regressed are listed in the figure caption of Figure 4 where the slopes read -2 , -2.08 and -2.10 for the reptation scheme, apparent linear plot and our model, respectively. Though the difference between them is not conspicuous, however, it is still detectable and the latter two show a clearer tendency of deviation from the first. This kind of deviation has been observed by many experimentalists and is obviously compatible with our scheme. A similar conclusion is reached for the diffusion constant of poly(butadiene) measured by the same authors⁹ and the result will be presented in combination with the related analysis of viscosity to display the effect of temperature on the exponential indices (see the discussion below).

Then we treat the case of short chain M in the Rouse regime. In this regime the motion of a chain as a whole is equivalent to its subchain due to the disappearance of entangling effect and thus we do not need to distinguish between the whole chain and its subchain. So the force F_c exerted on the chain and F_s on the subchain can be made equal, or $F_c = F_s$, under steady flow. Converted in the language of viscosity, it reads $\eta = \eta_s$. Reproducing here the result of η below M_c obtained in the precedent work¹

$$\eta = A_2 M \exp\left(\Delta E_0 - \frac{1}{2} \hbar \frac{a}{\sqrt{M}}\right) / k_B T, \quad (24)$$

where $A_2 = 4\pi^2 c_s^3 \hbar^3 K_0 / A k_B^2 M_c \theta_c^2$, and applying the Einstein relation once more, we have

$$D_s = K_0 k_B T / \eta_s = A_0 T M^{-1} \exp\left[-\left(\Delta E_0 - \frac{1}{2} \hbar \frac{a}{\sqrt{M}}\right) / k_B T\right]. \quad (25)$$

$A_0 = A k_B^3 M_c \theta_c^2 / 4\pi^2 c_s^3 \hbar^3$. As expected it is the same as D_c obtained previously¹ for $M < M_e$. Evidently, D_s of short chain scales as M^{-1} if the influence of the exponential part containing M is negligible,

$$D_s = D_{s0} M^{-1}. \quad (25a)$$

The prediction of eq. (25a) is well experimentally founded for conventional polymers and any deviation from it might be elucidated by the part ignored.

We briefly make two comments to stress the role of the term

$$\frac{1}{2} \hbar \frac{a}{k_B T \sqrt{M}}$$

playing on the deviation from the conventional predictions. Simply to ignore the term, our theory naturally predicts the behavior of the Rouse and reptation chains. It is self-evident that the term contains two parameters T and a , in addition to the variable M in the part

$$\frac{1}{2} \hbar \frac{a}{k_B T \sqrt{M}}$$

and we discuss their functions separately. (1) Owing to the adjustable parameter a appearing in the exponents of the relevant formulations like eq. (20) and (25) this theory explains a very broad spectrum of phenomena observed by resetting the value of a , even its sign (this point needs other investigation) when necessary. For instance, the stronger M -dependence of viscosity than 3.4-power is in the reach of our model.¹⁰ Detailed analysis on this subject is future work. (2) The influence of temperature (in connection with a and the range of M interested) on the magnitude of the power in the behavior of M -dependence of the dynamic quantities like D_s and η is reflected through varying the effective value of a in

$$\frac{1}{2} \hbar \frac{a}{k_B T \sqrt{M}}.$$

Taking the case of diffusion of poly(isoprene) analyzed above as example, it should show a stronger M -dependence at a lower temperature instead of $M^{-2.10(8)}$ in reality obtained at a higher temperature (373 K) which smears out the effect by diminishing the prefactor a_1 in eq. (20a). A quantitative comparison of the results of D_s and η is underway for poly(butadiene) and the tendency is seemingly in the right direction. Qualitatively, an increase in temperature should reduce the impact of the term on the indices of M -dependence, which will approach the values predicted from the Rouse model and the reptation or polymer mode coupling approaches at a very high temperature and the effect of the quantum constraints on the chain mobility is eliminated. A carefully prepared measurement of the same system at different temperatures should be able to detect such kind of the effect resulting from the confinement. The synergetic interaction of both T and a can also be taken into consideration. To get a better intuition, Figure 5 displays a qualitative comparison of the effect of T and a on the degree of D_s relying on M , separately. It is

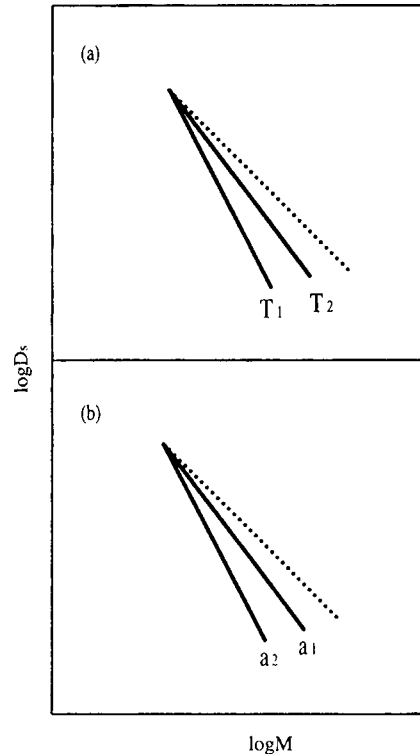


Figure 5 Schematic diagram showing the tendency of the temperature T and elastic interacting parameter a on the molecular dependence of diffusion constant in normal cases. (a) $T_1 < T_2$ at constant a ; (b) $a_1 < a_2$ at constant T . Dashed lines indicating the conventional predictions. At the stages of high molecular weight, the real lines develop towards the conventional values in the slopes (not shown in the figure).

worthy to note that the effect becomes weak in the range of high molecular weight, namely, it can be disregarded at the stage of large M . The above rationalization has implicitly assumed a non-zero a .

Along the same line of reasoning applied to viscosity, we analyze the effect of temperature on the diffusion coefficient D_s . We still take a high molecular weight as example, then from eq. (19) and (3) there is

$$D_s = C_{01} T^3 \exp \left\{ - \left(\Delta E_0 - \frac{1}{2} \hbar \frac{a}{\sqrt{M}} \right) / k_B T \right\} \quad (26)$$

where $C_{01} = MK_0 k_B / M_c C_{00}$. As argued above, the excitation relevant to the motion of a diffusing segment is frozen-in below T_g while the thermal fluctuation plays a role only above T_g , resulting in a shift of the "effective absolute temperature" from T to $T - T_g$. The equation (24) reads now in a modified form,

$$D_1 = C_{01}(T - T_g)^3 \times \exp\left\{-\left(\Delta E_0 - \frac{1}{2} \hbar \frac{a}{\sqrt{M}}\right) / k_B(T - T_g)\right\} \quad (27)$$

Defining a shifting factor a_T^D as a function of temperature

$$a_T^D = D_s(M, T, T_g) / D_s(M, T_0, T_g), \quad (28)$$

we deduce a scaling relation for diffusion, analogous to the WLF equation,

$$\log a_T^D = \frac{C_1^D(T - T_0)}{C_2^D + (T - T_0)}, \quad (29)$$

where

$$C_1^D = \frac{1}{2.303k_B(T_0 - T_g)} \left(\Delta E_0 - \frac{1}{2} \hbar \frac{a}{\sqrt{M}} \right) \quad (30a)$$

$$C_2^D = \frac{T_0 - T_g}{1 + \frac{3k_B(T_0 - T_g)}{\Delta E_0 - \frac{1}{2} \hbar \frac{a}{\sqrt{M}}}} \quad (30b)$$

This scaling relation differs from the equation (6) in sign and the second constant. The opposite signs in the both equations reflect the opposite tendency in D_s and η as a result of change in temperature. The constants C_1^D and C_2^D are dependent on the molecular weight M and glass transition temperature T_g , also on the reference temperature T_0 as well. At this point, it may be noted that the selection of T_0 influences the correlation of the experimental data. For a fixed system C_1^D and C_2^D are constants.

Terminal Relaxation Time τ_D and Young's Modulus

The relaxation time τ_D is another important quantity indexing the dynamics of a polymeric system and may be related to the other quantities discussed above. From the phenomenological theory, τ_D is connected to the viscosity through the steady-state compliance J_e^0 ,

$$\eta = (J_e^0)^{-1} \tau_D. \quad (31)$$

Experiments evidence a constant J_e^0 in the entangling regime. Consequently τ_D scales with the molecular weight M as η . It is interesting to notice that

as η scales as $M^{3.4}$, τ_D observes the same behavior, only differing in the prefactors,

$$\tau_D = \tau_{D0} M^{3.4} \quad (M > M_e). \quad (32)$$

Consequently, the inconsistency between experiments and other models disappears automatically in our theory. And also τ_D has a strong dependence on temperature and the WLF law is in principle applicable. The exact expression for it will be given later.

Eq. (31) can be derived from a molecular pointview by starting from the fundamental principle presumed in the previous work¹ and the reasoning above. For a high molecular weight, the conformation of a chain can be well described by the random walk model.¹¹ The radius of gyration may be given by

$$\langle R_g^2 \rangle = \frac{1}{6} C_\infty \frac{M}{m_0} l^2 \quad (33a)$$

$$= \frac{1}{6} C_\infty N l^2, \quad (33b)$$

where N is the number of the repeating units a chain contains and equals to M/m_0 , m_0 and l is the mass and length of the repeating unit, C_∞ is called the characteristic ratio, serving as a measure of the effect of short-range interaction, defined by

$$C_\infty = \lim_{n \rightarrow \infty} \langle r^2 \rangle_0 / \sum_i n_i l_i^2, \quad (33c)$$

where n_i is the number of the i th-kind bond of length l_i and $\langle r^2 \rangle_0$ is the unperturbed mean-square end-to-end distance. A chain takes a random flight and resumes a new position by going over a distance of $\langle R_g^2 \rangle^{1/2}$. This distance characterizes the critical state that there is just no overlapping between the mass centers of the old chain and the renewed. In other words, the memory of the original conformation message is completely lost after the chain has blindly walked over the characteristic distance of $\langle R_g^2 \rangle^{1/2}$. The interval of time ellipsed corresponds to τ_D . We are led to

$$\langle R_g^2 \rangle = 2D_s \tau_D. \quad (34)$$

(If we apply the relation of self-diffusion

$$D_G = \lim_{t \rightarrow \infty} \frac{1}{6t} \langle [\mathbf{R}_G(t) - \mathbf{R}_G(0)]^2 \rangle,$$

they differ in a factor of 3.) Setting eq. (19) and (33) into eq. (34), we obtain the following expression,

$$\begin{aligned}\tau_D &= \langle R_g^2 \rangle / 2D_s \\ &= \frac{1}{12K_0k_B T} C_\infty \frac{M_c}{m_0} l^2 \eta.\end{aligned}\quad (35)$$

All the numerical prefactors before η can be taken constant referring to M . A direct comparison of eq. (31) and (35) immediately reaches an interesting result

$$J_e^0 = \frac{1}{12K_0k_B T} C_\infty \frac{M_c}{m_0} l^2. \quad (36)$$

Undoubtedly, J_e^0 is molecular-weight independent. The polymer fluids will become soft as it cools and hard as we crosslink it by shortening the characteristic length of a typical segment. The inverse of J_e^0 is called the elastic modulus E

$$E = (J_e^0)^{-1}. \quad (37a)$$

Making use of eq. (36), it appears as

$$E = \frac{12K_0m_0}{C_\infty l^2} \frac{k_B T}{M_c}. \quad (37b)$$

It is clear that E is proportional to temperature T and depends inversely on the typical segment length M_c , relevant to the entangled statistical segment length M_e . To let ρ be

$$\frac{12K_0m_0}{C_\infty l^2},$$

eq. (37b) is reformulated as

$$E = \frac{\rho k_B T}{M_c}. \quad (37c)$$

If we explain the coefficient ρ in terms of the density of the transient network, eq. (37c) has the exact form as expected from the rubber theory.¹¹ Thus we retrieve the elastic modulus of a transient network from the master equation, without introducing the concept of affine deformation of the network.

Recalling eq. (3), the relaxation time τ_D expressible in

$$\begin{aligned}\tau_D &= 3.46 \times 10^{-2} C_\infty \frac{M_c}{K_0 k_B m_0} l^2 C_0 (T - T_g)^{-3} M^3 \\ &\times \exp \left[\left(\Delta E_0 - \frac{1}{2} \hbar \frac{a}{\sqrt{M}} \right) / k_B (T - T_g) \right],\end{aligned}\quad (38)$$

at a fixed high molecular weight M and scaled on temperature by a shift factor a_T^R of $\tau_D(M, T, T_g) / \tau_D(M, T_0, T_g)$ in a form, analogous to the WLF law,

$$\log a_T^R = - \frac{C_1^R (T - T_0)}{C_2^R + (T - T_0)}, \quad (39)$$

where C_1 and C_2 obey

$$C_1^R = \frac{1}{2.303 k_B (T_0 - T_g)} \left(\Delta E_0 - \frac{1}{2} \hbar \frac{a}{\sqrt{M}} \right) \quad (40a)$$

$$C_2^R = \frac{T_0 - T_g}{1 + \frac{3k_B(T_0 - T_g)}{\Delta E - \frac{1}{2} \hbar \frac{a}{\sqrt{M}}}}. \quad (40b)$$

Finally it is of necessity to point out that η , D_s and τ_D may also display a scaling behavior of temperature dependence in the regime of short chain, similar to the WLF equation but with modified constants.

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