Dynamic theory of polymer melts. Reptation as a dynamic phase transition

V. G. Rostiashvili

Branch of the Institute of Chemical Physics, Academy of Sciences of the USSR

A generating Dominicis–Peliti functional is derived: It generates time correlation functions for a melt of a system of polymer chains interacting with the Edwards Hamiltonian. The Gaussian approximation is used to obtain an expression for the correlation functions and susceptibilities. The concept of a local anisotropy of the mutual repulsion of chains is substantiated, together with the susceptibilities which are tangential or lateral relative to a profile of a polymer chain. A nonlinear approximation for the lateral self-diffusion coefficient is obtained in the principal approximation describing the interaction of a test chain with a polymer medium. It is shown that this equation has a solution corresponding to a localized state and that the localization length plays the role of the order parameter. In the limit of long chains the new theory is equivalent to the tube model. An explicit expression is obtained for the thickness of a tube expressed in terms of the chain characteristics.

1. INTRODUCTION

Modern dynamic theory of polymer melts relies strongly on the concept of chain cross-links formed because the chains do not intersect. The main model assumption[1,2] is that cross-links prevent the motion of a chain at right-angles to the line of its contour; a chain moves along its contour inside a tube formed by the cross-links (the motion of a chain then resembles the creeping motion of a snake and is known as reptation).

The microscopic reason for the concept of a tube is the local anisotropy of the mutual repulsion between chains, first pointed out in Ref. 3. The local anisotropy of this interaction is a consequence of the invariance of this energy in the course of translation of a macromolecule along its contour, i.e., the interaction force is orthogonal to the chain contour.

We shall develop these ideas in the present paper in a fairly general form and then apply them to investigate the self-diffusion coefficient of a macromolecule in a melt. This will be done by the Lagrangian formulation of the dynamic problem of a system of polymer chains interacting in accordance with the Edwards Hamiltonian (Sec. 2). The principal (leading) approximation will be used to obtain expressions for the complete density correlation function. The concept of a local anisotropy of the bulk interaction, introduced in Sec. 3, leads to the idea of longitudinal and transverse (relative to a polymer chain profile) susceptibilities. The diffusion approximation describing the longitudinal motion and generalizing the corresponding equation for a primitive chain[2] will be derived. The skeleton theory of perturbations (Sec. 4) will be used to obtain an equation for the coefficient $D^\perp(\mathbf{k}, z)$ of transverse diffusion causing dispersion. It will be shown in Sec. 5 that this equation describes a dynamic transition of the localization–delocalization type, which in the case of polymers represents a transition from the Rouse behavior to reptation. We shall use here the ideas and representations developed earlier within the framework of nonlinear fluctuation hydrodynamics employed by Götze.[4,5] Localization occurs for a certain critical chain length N_c. We shall analyze expressions for the localization length d_0 at right-angles to the chain contour. The localization length tube d_0 clearly corresponds to the tube thickness in the reptation model of Refs. 1 and 2, but in contrast to the tube it is a rigorously defined and readily described concept. The quantity d_0 can be expressed in terms of the characteristics of a test chain, the interaction potential, and the correlation function of a polymer medium. The final result is obtained for the case when a test chain is moving in a frozen polymer medium, but the theory can be applied also more generally. We shall assume that in the case of the system under consideration we can ignore the hydrodynamic interaction, so that we shall not discuss it here.

2. LAGRANGIAN FORMULATION OF FLUCTUATION HYDRODYNAMICS FOR A SYSTEM OF INTERACTING CHAINS

We shall adopt a continuum model of a chain of length N and describe its position in space by specifying the function $R_j^\alpha(\tau, t)$ representing the radius vector of an element of the α th chain at a moment t located at a distance $\tau(0 \leqslant \tau \leqslant N)$ from its end. The stochastic dynamics of a system of n interacting chains is then described by

$$\frac{\partial}{\partial t} R_j^\alpha(\tau, t) = \zeta_0^{-1} \frac{\delta H\{R_j\}}{\delta R_j^\alpha(\tau, t)} + f_j^\alpha(\tau, t), \quad \alpha = 1, \ldots, n,$$

(2.1)

where ζ_0 is the "unrenormalized" (bare) friction coefficient of a chain segment; $f_j^\alpha(\tau, t)$ is a random Gaussian force with the zero average, and the Hamiltonian $H\{R_j\}$ has the Edwards form:[6]

$$H\{R_j\} = \frac{3}{2} \sum_{\alpha=1}^{n} \int_0^{N} d\tau \left(\frac{\partial R_j^\alpha}{\partial \tau} \right)^2$$

$$+ \frac{1}{2} \sum_{\alpha=1}^{n} \sum_{\beta=1}^{n} \int_0^{N} d\tau \int_0^{N} d\tau' \, V[\mathbf{R}^\alpha(\tau, t) - \mathbf{R}^\beta(\tau', t)],$$

(2.2)

where the length of a Kuhn segment l is taken to be unity. The first term describes the elastic energy of the interacting chains and the second the mutual repulsion between them (the actual nature of the interaction will be discussed in greater detail later).

A fluctuation hydrodynamics of a system described by Eqs. (2.1) and (2.2) will be based on the results of Refs. 7 and 8 where a generating functional is obtained for the time-dependent Ginzburg–Landau model. Integration in the generating functional is carried out over a field $R_j^\alpha(\tau, t)$ and over an auxiliary field $\hat{R}_j^\alpha(\tau, t)$, whereas the effective action for the problem described by Eqs. (2.1) and (2.2) is

$$A\{R_j^\alpha \; \hat{R}_j^\alpha\} = \sum_{\alpha=1}^{n} \int dt \, d\tau \Big\{ -\zeta_0 T [\hat{R}_j^\alpha]^2$$

$$+ i\hat{R}_j^\alpha \Big[\zeta_0 \frac{\partial R_j^\alpha}{\partial t} - 3 \frac{\partial^2 R_j^\alpha}{\partial \tau^2}$$

$$+ \tfrac{1}{2} \sum_{\beta=1}^{n} \int d\tau' \int \frac{d^3 k}{(2\pi)^3} \, ik_j V(\mathbf{k}) \exp\{i\mathbf{k}[\mathbf{R}^\alpha(\tau, t)$$

$$-\mathbf{R}^\beta(\tau', t)]\} \Big] \Big\}.$$

(2.3)

The diagrams generated by the action (2.3) contain two types of line: correlation functions $\langle R_i^\alpha(\tau, t) R_j^\beta(\tau', t') \rangle$ and the response functions $\langle \hat{R}_i^\alpha(\tau, t) R_j^\beta(\tau', t') \rangle$, where

$$\langle \hat{R}_i^\alpha(\tau, t) \hat{R}_j^\beta(\tau', t') \rangle = 0.$$

The Jacobian which appears in the functional integral can be ignored if we also ignore the diagrams containing a closed loop $\langle \hat{R}_i^\alpha(\tau, t) R_j^\beta(\tau, t) \rangle$.[7,8]

We shall be interested in the space–time correlation functions of the density and in the corresponding susceptibility. We shall therefore adopt local densities

$$\rho(\mathbf{r}, t) = \sum_{\alpha=1}^{n} \int_0^N d\tau \, \delta(\mathbf{r} - \mathbf{R}^\alpha(\tau, t)),$$

(2.4a)

$$\pi_j(\mathbf{r}, t) = \sum_{\alpha=1}^{n} \int_0^N d\tau \, i\hat{R}_j^\alpha(\tau, t) \delta(\mathbf{r} - \mathbf{R}^\alpha(\tau, t)).$$

(2.4b)

Then, the generating functional with the action defined by (2.3) becomes

$$Z\{\ldots\} = \int DR_j^\alpha \, D\hat{R}_j^\alpha \, D\pi_j D\rho \, \delta \Big[\rho(\mathbf{r}, t)$$

$$- \sum_{\alpha=1}^{n} \int d\tau \, \delta(\mathbf{r} - \mathbf{R}^\alpha(\tau, t)) \Big]$$

$$\times \delta \Big[\pi_j(\mathbf{r}, t) - \sum_{\alpha=1}^{n} \int d\tau \, i\hat{R}_j^\alpha \delta(\mathbf{r} - \mathbf{R}^\alpha(\tau, t)) \Big]$$

$$\times \exp\Big\{ -\tfrac{1}{2} \int dt \int d^3 r_1 \int d^3 r_2 \, \pi_j(\mathbf{r}_1, t) \rho(\mathbf{r}_1, t)$$

$$\times (-i\nabla_j) V(\mathbf{r}_1 - \mathbf{r}_2) - A_0 \Big\},$$

(2.5)

where $A_0\{R_j^\alpha, \hat{R}_j^\alpha\}$ is the action of a system of free chains.

Using the integral representation for the δ functions and going over to four-dimensional variables

$$\bar{\rho}_\alpha = \begin{pmatrix} \rho \\ \pi_j \end{pmatrix}, \quad \bar{\psi}_\alpha = \begin{pmatrix} \psi \\ \varphi_j \end{pmatrix}, \quad \bar{R}_\alpha = \begin{pmatrix} 1 \\ \hat{R}_j \end{pmatrix},$$

we find that integration with respect to ρ and π_j gives the compact form

$$Z\{\ldots\} = \int D\bar{\psi}_\alpha \exp\Big\{ n \ln K\{\bar{\psi}\} - \int_{1,2} \bar{\psi}_\alpha(1) U_{\alpha\beta}^{-1}(1, 2) \bar{\psi}_\beta(2) \Big\},$$

(2.6)

where

$$K\{\bar{\psi}_\alpha\} = \Big\langle \exp\Big\{ -i \int d\tau \, dt \, \bar{R}_\alpha(\tau, t) \bar{\psi}_\alpha(R_j(\tau, t)) \Big\} \Big\rangle_0,$$

(2.6a)

and the four-matrix is

$$U_{\alpha\beta} = \begin{pmatrix} 0 & -\nabla_j V \\ \nabla_j V & 0 \end{pmatrix}.$$

(2.6b)

Moreover, we can quite simply find the exact relationship between the correlation functions of the observed variable $\bar{\rho}_\alpha$ and the auxiliary variable $\bar{\psi}_\alpha$:

$$\langle \bar{\rho}_\alpha(1) \bar{\rho}_\beta(2) \rangle$$

$$= 2U_{\alpha\beta}^{-1}(1, 2) - 4 \int_{3,4} U_{\alpha\omega}^{-1}(1, 3) U_{\beta\gamma}^{-1}(2, 4) \langle \bar{\psi}_\omega(3) \bar{\psi}_\gamma(4) \rangle.$$

(2.7)

The relationships (2.6)–(2.7) are generalizations, to the case of dynamics, of the expressions obtained for the partition functions of a semidilute polymer solution.[9] Following Ref. 9, we find that an analysis of the dimensionality shows that expansion of $\ln K\{\bar{\psi}_\alpha\}$ in powers of $\bar{\psi}_\alpha$ gives rise to perturbation theory expressions with the parameter of the expansion $v_0 N^{2-d/2}$ for the fixed value of $n^* v_0 N^2$, where v_0 is the excluded volume, d is the dimensionality of space, $n^* = n/\Omega$, and Ω is the volume of the system.

In particular, if we use the Gaussian approximation, we obtain

$$n \ln K\{\bar{\psi}_\alpha\} = -n^* \int_{1,2} \bar{\psi}_\alpha(1) \bar{\psi}_\beta(2) \Gamma_{\alpha,\beta}(1, 2),$$

(2.8)

where

$$\Gamma_{\alpha\beta}(1, 2) = \tfrac{1}{2} (2\pi)^d \delta(k_1 + k_2) \Gamma_{\alpha\beta}(k_1; t_1, t_2)$$

$$= \tfrac{1}{2} (2\pi)^d \delta(k_1 + k_2)$$

$$\times \int_{\tau_1, \tau_2} \Big\langle \bar{R}_\alpha(\tau_1, t_1) \bar{R}_\beta(\tau_2, t_2) \exp\Big[i \sum_{p=1}^{2} k_j^p R_j(\tau_p, t_p) \Big] \Big\rangle$$

(2.8a)

and $\langle \ldots \rangle_0$ is the average for a system of free chains.

Using the Gaussian approximation of Eq. (2.8) in Eq. (2.6), we find from Eq. (2.7) that

$$\langle \bar{\rho}_\alpha(1) \; \bar{\rho}_\beta(2) \rangle = 2 [(n^* \hat{\Gamma})^{-1} + U]_{\alpha\beta}^{-1}.$$

(2.9)

The four-matrix $\hat{\Gamma}_{\alpha\beta}$, which describes completely the dynamics of an isolated chain, has the block structure

$$\hat{\Gamma}_{\alpha\beta}(k; t_1, t_2) = \begin{pmatrix} (\Gamma_{00}) & (\Gamma_{01}\Gamma_{02}\Gamma_{03}) \\ \begin{pmatrix} \Gamma_{10} \\ \Gamma_{20} \\ \Gamma_{30} \end{pmatrix} & (\Gamma_{rq}) \end{pmatrix}, \qquad (2.10)$$

where

$$r, q = 1, 2, 3; \quad \Gamma_{rq} \equiv 0. \qquad (2.10a)$$

In fact, a pair of Gaussian random fields $R_j^{\alpha}(\tau,t)$ and $\hat{R}_j^{\alpha}(\tau,t)$ is described by the following expression dealing with separation of the correlation functions[10]

$$\langle \hat{R}_j^{\alpha}(\tau, t) \mathscr{L}\{R_l^{\beta}\} \rangle_0$$

$$= \int d\tau' \, dt' \langle \hat{R}_j^{\alpha}(\tau, t) R_l^{\beta}(\tau', t') \rangle_0 \left\langle \frac{\delta \mathscr{L}\{R_l^{\beta}\}}{\delta R_l^{\beta}(\tau', t')} \right\rangle_{\cdot q},$$

$$(2.11)$$

where $\mathscr{L}\{R_l^{\beta}\}$ is a generating functional; repeated indices imply summation. Then, applying twice Eq. (2.11), we obtain

$$\Gamma_{rq} = -k_m k_n \int d\tau_1 \, d\tau_2 \langle R_m(\tau_1, t_1) \hat{R}_r(\tau_2, t_2) \rangle_0$$

$$\times \langle R_n(\tau_2, t_2) \hat{R}_q(\tau_1, t_1) \rangle_0$$

$$\times \exp\{-\tfrac{1}{6}k^2 \langle [R(\tau_1, t_1) - R(\tau_2, t_2)]^2 \rangle_0\}.$$

The identity given in Eq. (2.10a) then follows from the delayed nature of the response functions:

$$\langle R_i(t_2) \hat{R}_j(t_1) \rangle_0 \sim \theta(t_1 - t_2), \quad \langle R_i(t_2) \hat{R}_j(t_1) \rangle_0 \sim \theta(t_2 - t_1).$$

The remaining diagonal and off-diagonal terms of the matrix (2.10) are related by expressions that follow from the fluctuation—dissipation theorem (FDT) described in Refs. 7 and 8:

$$-\frac{\partial}{\partial t} \langle R_i(\tau, t) R_j(\tau', t') \rangle$$

$$= T[\langle R_i(\tau, t) \hat{R}_j(\tau', t') \rangle - \langle R_i(\tau', t') \hat{R}_j(\tau, t) \rangle]. \qquad (2.12)$$

If we separate the correlation functions again by means of Eq. (2.11), we obtain

$$\Gamma_{j0}(\mathbf{k}; t_1 - t_2)$$

$$= ik_m \int_{\tau_1, \tau_2} \langle \hat{R}_j(\tau_1, t_1) R_m(\tau_2, t_2) \rangle_0 \exp\{-\tfrac{1}{6}k^2 \langle [R(\tau_1, t_1)$$

$$- R(\tau_2, t_2)]^2 \rangle_0\} = \frac{ik_j}{Tk^2} \frac{\partial}{\partial t_1} \Gamma_{00}(\mathbf{k}; t_1 - t_2), \quad t_1 < t_2$$

$$(2.13)$$

[the FDT of Eq. (2.12) is used here].
Similar transformations give

$$\Gamma_{j0}(\mathbf{k}; t_1 - t_2) = -\frac{ik_j}{Tk^2} \frac{\partial}{\partial t_1} \Gamma_{00}(\mathbf{k}; t_1 - t_2), \quad t_2 < t_1. \qquad (2.13a)$$

Combining Eqs. (2.13) and (2.13a) and applying the time Fourier transformation, we obtain

$$-\frac{i\omega}{T} \Gamma_{00}(k, \omega) = ik_j \Gamma_{0j}(k, \omega) - ik_j \Gamma_{j0}(\mathbf{k}, \omega). \qquad (2.14)$$

Moreover, in view of the stationary nature of the correlation functions, we have

$$\Gamma_{0j}(-\omega) = \Gamma_{j0}(\omega), \quad \Gamma_{00}(-\omega) = \Gamma_{00}(\omega). \qquad (2.14a)$$

The correlation matrix of Eq. (2.9) is

$$\langle \bar{\rho}_\alpha(1) \bar{\rho}_\beta(2) \rangle = \begin{pmatrix} \langle \rho(1)\rho(2) \rangle & \langle \rho(1)\pi_j(2) \rangle \\ \langle \pi_j(1)\rho(2) \rangle & 0 \end{pmatrix}, \qquad (2.15)$$

where zero means the 3×3 matrix, the element $\langle \rho(1)\rho(2) \rangle$ is a density correlation function, $\langle \pi_j(1)\rho(2) \rangle$ is the retarded susceptibility, and $\langle \rho(1)\pi_j(2) \rangle$ is the advanced susceptibility. As usual, the susceptibilities are obtained if Eq. (2.1) is supplemented by an external force $\varkappa_j(\mathbf{r},t)$:

$$\frac{\delta H}{\delta R_i} \to \frac{\delta H}{\delta R_i} - \varkappa_j(R(\tau, t)),$$

and if the source term

$$i \int d^3 r \, \chi(\mathbf{r}, t) \rho(\mathbf{r}, t)$$

is added in the expression describing the action. We then have

$$S(1, 2) \equiv \langle \rho(1)\rho(2) \rangle = -Z^{-1}\{0\} \frac{\delta^2}{\delta\chi(1)\delta\chi(2)} Z\{\varkappa_j, \chi\},$$

$$(2.16)$$

$$G_j^{(+)}(1, 2) \equiv \langle \pi_j(1)\rho(2) \rangle$$

$$= -Z^{-1}\{0\} \frac{\delta^2}{\delta\varkappa_j(1)\delta\chi(2)} Z\{\varkappa_j, \chi\}, \quad t_1 < t_2,$$

$$(2.16a)$$

$$G_j^{(-)}(1, 2) \equiv \langle \pi_j(2)\rho(1) \rangle$$

$$= -Z^{-1}\{0\} \frac{\delta^2}{\delta\varkappa_j(2)\delta\chi(1)} Z\{\varkappa_j, \chi\}, \quad t_1 > t_2.$$

$$(2.16b)$$

In the case of the density correlations the external force is usually the pressure p, where $\varkappa_j = -\nabla_j p$. Then, the density–pressure susceptibilities become

$$G^{(+)} = ik_j \Gamma_{0j}, \quad G^{(-)} = ik_j \Gamma_{j0},$$

and the matrix of Eq. (2.10) is replaced with the following 2×2 matrix

$$\mathbf{G} = \begin{pmatrix} \Gamma_{00} & G^{(+)} \\ G^{(-)} & 0 \end{pmatrix}. \qquad (2.17)$$

The interaction matrix of Eq. (2.6b) also becomes a 2×2 matrix and in the k-representation it is described by

$$\mathbf{U} = \begin{pmatrix} 0 & -k^2 V(k) \\ k^2 V(k) & 0 \end{pmatrix}. \qquad (2.18)$$

Inversion of the matrices in Eq. (2.9) and separation of the nonzero diagonal element, gives the following expression for the density correlation function

$$S(\mathbf{k}, \omega) = 2n^* \Gamma_{00} [1 - in^* V k_j \Gamma_{j0}]^{-1} [1 - in^* V k_j \Gamma_{0j}]^{-1}.$$

(2.19)

Similar calculations for the off-diagonal elements give the following expressions:

$$G_j^{(+)}(\mathbf{k}, \omega) = 2n^* \Gamma_{0j} [1 - in^* V k_j \Gamma_{0j}]^{-1},$$ (2.20)

$$G_j^{(-)}(\mathbf{k}, \omega) = -2n^* \Gamma_{j0} [1 - in^* V k_{j0} \Gamma_{j0}]^{-1},$$ (2.20a)

$$G_j^{(+)}(-\omega) = -G_j^{(-)}(\omega).$$ (2.20b)

We can see that the FDT for isolated chains [Eq. (2.14)] guarantees the Gaussian-approximation FDT for a melt:

$$-\frac{i\omega}{T} S(\mathbf{k}, \omega) = ik_m G_m^{(+)}(\mathbf{k}, \omega) + ik_m G_m^{(-)}(\mathbf{k}, \omega).$$ (2.21)

Using the thermodynamic sum rule

$$\Gamma_{j0}(\omega = 0) = \Gamma_{0j}(\omega = 0) = \frac{ik_j}{Tk^2} \Gamma_{00}(t = 0),$$

we can obtain directly the expression for the static correlation function

$$S_{st}(\mathbf{k}) = \frac{2n^* \Gamma_{00}(\mathbf{k}, t = 0)}{1 + n^* V(k) \Gamma_{00}(\mathbf{k}, t = 0)/T}.$$ (2.22)

If we introduce the direct correlation function $\Phi(\mathbf{k}) = -V(\mathbf{k})/2T$ used in the theory of liquids,[11] we find that Eqs. (2.20) and (2.22) are analogous to the results obtained in the mean-field approximation.[12,13]

3. LOCAL ANISOTROPY OF THE REPULSIVE INTERACTION

The tube concept in the reptation model[1,2] reflects an intuitively obvious fact that the mobility of a chain in a polymer melt is locally anisotropic. A chain moves along the line of its contour practically unhindered because segments from other chains cannot penetrate between a pair of adjacent segments. This is true also of computer modeling of the reptatory motion.[14,15] However, the motion in the lateral (i.e., normal to the line of the chain profile direction) is greatly hindered by the mutual repulsion of the chains. Although the motion along the chain profile is accompanied by fluctuations of the interaction energy, we shall consider that the motion is averaged over these fluctuations and postulate that the averaging scale is much smaller than the length of a statistical chain segment.

Following Ref. 3, we shall introduce the components of the radius vector $\mathbf{R}_i(\tau)$ which are tangential

$$R_i^{\|}(\tau) = (R_l(\tau) e_l(\tau)) e_i(\tau)$$ (3.1)

and normal

$$R_i^{\perp}(\tau) = R_i(\tau) - R_i^{\|}(\tau)$$ (3.1a)

to the chain contour and assume that a unit tangential vector at the point $R_i(\tau)$ is

$$e_i(\tau) = \partial_\tau R_i(\tau)/|\partial_\tau R_i(\tau)|.$$ (3.1b)

Then the condition for unhindered motion of a chain along the line of its contour is equivalent to the invariance of the exchange interaction energy in the Hamiltonian of Eq. (2.2) in the case of an infinitesimal transformation of the coordinates of a test chain

$$R_i^\alpha(\sigma) \to R_i^\alpha(\sigma) - \varepsilon^\alpha(\sigma) \partial_\sigma R_i^\alpha(\sigma).$$ (3.2)

We can easily show that in the case of an arbitrary infinitesimal function $\varepsilon^\alpha(\sigma)$ the condition of Eq. (3.2) gives zero value for the tangential component of the force

$$\partial_\tau \int d\sigma \sum_{\beta=1}^n V[\mathbf{R}^\alpha(\tau) - \mathbf{R}^\beta(\sigma)] = 0.$$ (3.3)

Then the term corresponding to the bulk interaction in Eq. (2.3) becomes

$$\frac{1}{2} \sum_{\alpha,\beta} \int dt \, d\tau \, d\sigma \, i\dot{R}_j^\alpha(\tau, t) \Delta_{ji}^\perp(\tau, t)$$
$$\times \frac{\delta}{\delta R_i^\alpha(\tau, t)} V[R_i^\alpha(\tau, t) - R_i^\beta(\sigma, t)],$$ (3.4)

where the force projection operator in the normal direction is

$$\Delta_{ji}^\perp(\tau, t) = \delta_{ji} - \frac{\partial_\tau R_j(\tau, t) \partial_\tau R_i(\tau, t)}{|\partial_\tau R_i(\tau, t)|^2},$$ (3.4a)

and the additional projection operator

$$\Delta_{ji}^{\|}(\tau, t) = \frac{\partial_\tau R_j(\tau, t) \partial_\tau R_i(\tau, t)}{|\partial_\tau R_i(\tau, t)|^2}$$ (3.4b)

has the following properties:

$$\Delta^\perp + \Delta^{\|} = 1, \quad (\Delta^\perp)^2 = \Delta^\perp, \quad (\Delta^{\|})^2 = \Delta^{\|}, \quad \Delta^\perp \Delta^{\|} = 0.$$ (3.4c)

Infinitesimal displacements of the chain elements in the normal direction give rise to tangential displacements of a higher order of smallness. Since tangential displacements are related solely to the elastic forces, it follows that in the harmonic approximation of Eq. (2.2) we can assume that the normal and tangential variables are separable. In this case the total susceptibility of Eq. (2.16a) can be represented in the form

$$\langle \pi_j(1) \rho(2) \rangle = \langle \pi_j^\perp(1) \rho(2) \rangle + \langle \pi_j^{\|}(1) \rho(2) \rangle$$
$$= -Z_\perp^{-1}\{0\} \frac{\delta^2 Z_\perp\{x_j; \chi\}}{\delta x_j(1) \delta \chi(2)} - Z_{\|}^{-1}\{0\} \frac{\delta^2 Z_{\|}\{x_j, \chi\}}{\delta x_j(1) \delta \chi(2)},$$

(3.5)

where

$$\pi_j^{\perp, \|}(\mathbf{r}, t) = \int d\sigma \, \Delta_{ji}^{\perp, \|}(\sigma, t) \dot{R}_i(\sigma, t) \delta(\mathbf{r} - \mathbf{R}(\sigma, t)).$$

(3.5a)

The expression for the tangential generating functional is unrelated to the bulk interaction and is of the form

$$Z_{\|}\{x_j, \chi\} = \Big\langle \exp\Big\{ i \int dt \, d\tau [\chi(R_j(\tau, t))$$
$$+ \Delta_{ji}^{\|}(\tau, t) \dot{R}_i(\tau, t) x_j(R_j(\tau, t))] \Big\} \Big\rangle_0.$$

(3.6)

Calculations of the normal generating functional $Z_\perp\{x_j, \chi\}$, the form of which is determined largely by the bulk repulsive

interaction, will be reported in the next section.

We can demonstrate more clearly the nature of the tangential (curvilinear) motion of a test chain by obtaining the diffusion equation representing such motion.[2] We shall consider the tangential susceptibility of a test chain

$$G^{\parallel}(\mathbf{k}; \tau_1, \tau_2; t_1, t_2) = \langle \hat{R}_l(\tau_2, t_2) i k_j{}^2 \partial_{\tau_s} R_j(\tau_2, t_2) \partial_{\tau_s} R_l(\tau_2, t_2)$$

$$\times \exp\left[i \sum_{p=1}^{2} k_j{}^p R_j(\tau_p, t_p)\right]\rangle_0 \Big|_{k_j{}^1 = -k_j{}^2 = k_j}$$

$$= \frac{1}{3T} \langle \hat{R}_l(\tau_2, t_2) R_l(\tau_1, t_1) \rangle_0$$

$$\times \left\langle [ik_j{}^2 \partial_{\tau_s} R_j(\tau_2, t_2)]^2 \exp\left[i \sum_{p=1}^{2} k_j{}^p R_j(\tau_p, t_p)\right]\right\rangle_0 \Big|_{k_j{}^1 = -k_j{}^2 = k_j}$$

$$= -\frac{1}{6T}\frac{\partial}{\partial t_2}\langle[R_j(\tau_1, t_1) - R_j(\tau_2, t_2)]^2\rangle_0 \{\langle \partial_{\tau_s}{}^2 \exp[\cdots]_0\rangle$$

$$\qquad - \langle i k_j \partial_{\tau_s}{}^2 R(\tau_2, t_2) \exp[\cdots]\rangle_0\}, \qquad (3.7)$$

where the rule for separation of the Gaussian fluctuations of Eq. (2.11) and the FDT of Eq. (2.12) are used. Since

$$|\partial_\tau R_j(\tau, t)|^2 = 1,$$

$$\langle \partial_\tau R_j(\tau, t) R_j(\tau, t)\rangle_0 = \langle \partial_\tau{}^2 R_j(\tau, t) R_j(\tau, t)\rangle_0 = 0,$$

it follows that the second term in the braces in Eq. (3.7) must vanish.

The averaging in Eq. (3.7) involves the tangent and curvature at the point $\tau = \tau_2$, so that we cannot transpose the operations of taking the second derivative $\partial_{\tau_2}^2$ and averaging

$$\langle \ldots \rangle_0 = \int DR_j\, d\hat{R}_j \ldots \exp\{-A_0\{\mathbf{R}, \hat{\mathbf{R}}\}\}. \qquad (3.8)$$

Therefore, the averaging procedure of Eq. (3.8) must be represented as consecutive integration in the normal and tangential subspaces:

$$\langle \ldots \rangle_0 = \langle\langle \ldots \rangle_0{}^{\parallel}\rangle_0{}^{\perp}, \qquad (3.9)$$

where

$$\langle \ldots \rangle_0{}^{\parallel} = \int DR_j{}^{\parallel} D\hat{R}_j{}^{\parallel} \ldots \exp\{-A_0\{\mathbf{R}^{\parallel}, \hat{\mathbf{R}}^{\parallel}\}\}, \qquad (3.9a)$$

$$\langle \ldots \rangle_0{}^{\perp} = \int DR_j{}^{\perp} D\hat{R}_j{}^{\perp} \ldots \exp\{-A_0\{\mathbf{R}^{\perp}, \hat{\mathbf{R}}^{\perp}\}\}. \qquad (3.9b)$$

The operations $\partial_{\tau_2}^2$ and $\langle \ldots \rangle_0^{\parallel}$ can be transposed, because integration in the tangential subspace does not result in the loss of the tangent and curvature at the point $\tau = \tau_2$. On the other hand, since the motion of a chain in the normal subspace is localized on a scale equal to the tube thickness (see Sec. 5), the averaging described by $\langle \ldots \rangle_0^{\perp}$ is in fact carried out over the bends of the real circuit near the average line of the tube representing a primitive chain (using the terminology of Ref. 2). Such averaging is carried out over the times $t \leqslant \tau_{\text{Rouse}} \sim N^2$.

Therefore, the first term in the braces of Eq. (3.7) becomes

$$\langle \partial_{\tau_2}{}^2 \langle \exp\{ik_j[R_j(\tau_2, t_2) - R_j(\tau_1, t_1)]\}\rangle_0{}^{\parallel}\rangle_0{}^{\perp}$$

$$= \partial_{\xi_2}{}^2 \langle \exp\{ik_j[R_j(\xi_2, t_2) - R_j(\xi_1, t_1)]\}\rangle_0{}^{\parallel}, \qquad (3.10)$$

where ξ is the contour variable of the primitive chain, where $\xi_1 = \xi_1(\tau_1)$ and $\xi_2 = \xi_2(\tau_2)$. Thus, Eq. (3.7) yields

$$G^{\parallel}(\mathbf{k}; \tau_1, \tau_2; t_1, t_2) = -\frac{D_0}{T}\frac{\partial^2}{\partial \xi_2{}^2}\Pi(\mathbf{k}; \xi_1, \xi_2; t_1, t_2), \qquad (3.11)$$

where

$$\Pi(\mathbf{k}; \xi_1, \xi_2; t_1, t_2) = \langle \exp\{ik_j[R_j(\xi_2, t_2) - R_j(\xi_1, t_1)]\}\rangle_0{}^{\parallel}, \qquad (3.11a)$$

and

$$D_0 = \frac{1}{6}\frac{\partial}{\partial t_2}\langle[R_j(\tau_1, t_1) - R_j(\tau_2, t_2)]^2\rangle \qquad (3.11b)$$

is the Rouse self-diffusion coefficient. In the low-frequency limit we have $D_0 = \tilde{D}_0 / N$, where $\tilde{D}_0$ is a quantity of the order of the self-diffusion coefficient for a monomer melt.

On the other hand, the FDT for the tangential susceptibility gives

$$G^{\parallel}(\mathbf{k}; \tau_1, \tau_2; t_1, t_2) = -\frac{1}{T}\frac{\partial}{\partial t_2}\Pi. \qquad (3.12)$$

A comparison of Eqs. (3.11) and (3.12) yields the diffusion equation for a primitive chain[2]

$$\frac{\partial}{\partial t}\Pi = D_0\frac{\partial^2}{\partial \xi^2}\Pi. \qquad (3.13)$$

The expression for the Laplace transform of a tangential correlation function of the density in the hydrodynamic (low-frequency) limit[16] is of the form

$$S^{\parallel}(\mathbf{k}, z) = \int_0^{\infty} dt\, e^{izt} \int_0^{N_0} d\xi_1 \int_0^{N_0} d\xi_2 \Pi(\mathbf{k}; \xi_1, \xi_2; t)$$

$$= \frac{\frac{1}{3}S_{st}(k)}{-iz + k^2 D^{\parallel}(\mathbf{k}, z)}, \qquad (3.13)$$

where $N_0 \sim N$ is the length of a primitive chain; $D^{\parallel}(k,z)$ is the self-diffusion coefficient of a chain undergoing reptatory motion and described in the low-frequency limit by $D^{\parallel} = \tilde{D}_0/N^2$ (Refs. 1 and 2); $S_{st}(k)$ is the static density correlation function. The explicit expressions for the Laplace transform $\Pi(\mathbf{k}; \xi_1, \xi_2, t)$ and for the dispersive self-diffusion coefficient $D^{\parallel}(\mathbf{k}, z)$ can be found in Ref. 12.

In addition to the tangential (reptatory) motion, we have to consider also the normal (lateral) motion. In particular, it follows from Eq. (3.5) that the total susceptibility G consists of the tangential $G^{\parallel}$ and normal $G^{\perp}$ susceptibilities. In the hydrodynamic limit[16] this representation becomes

$$G(\mathbf{k}, z) = G^{\parallel}(\mathbf{k}, z) + G^{\perp}(\mathbf{k}, z). \qquad (3.15)$$

Here,

$$G(\mathbf{k}, z) = \frac{k^2 D_s(\mathbf{k}, z)}{-iz + k^2 D_s(\mathbf{k}, z)} G_{st}(\mathbf{k}), \qquad (3.15a)$$

$$G^{\parallel}(\mathbf{k}, z) = \frac{k^2 D^{\parallel}(\mathbf{k}, z)}{-iz + k^2 D^{\parallel}(\mathbf{k}, z)} \cdot \frac{1}{3}G_{st}(\mathbf{k}), \qquad (3.15b)$$

$$G^{\perp}(\mathbf{k}, z) = \frac{k^2 D^{\perp}(\mathbf{k}, z)}{-iz + k^2 D^{\perp}(\mathbf{k}, z)} \cdot \frac{2}{3}G_{st}(\mathbf{k}), \qquad (3.15c)$$

where $G_{st}(\mathbf{k}) = S_{st}(\mathbf{k})/T$, $D_s(\mathbf{k}, z)$ is the self-diffusion coefficient of a test chain and $D^{\perp}(\mathbf{k}, z)$ is the coefficient repre-

senting the motion of segments of this test chain along the normal directions. In the next section we shall show that vanishing of $D^{\perp}(\mathbf{k},z)$ represents a transition from the Rouse motion to reptation. It follows from Eqs. (3.15)–(3.15c) that a similar representation applies to the autocorrelation density functions

$$S(\mathbf{k}, z) = S^{\parallel}(\mathbf{k}, z) + S^{\perp}(\mathbf{k}, z), \qquad (3.16)$$

where

$$S(\mathbf{k},z) = \frac{S_{st}(\mathbf{k})}{-iz + \mathbf{k}^2 D_s(\mathbf{k}, z)}, \qquad (3.16a)$$

$$S^{\parallel}(\mathbf{k},z) = \frac{{}^{1}/_{3}S_{st}(\mathbf{k})}{-iz + \mathbf{k}^2 D^{\parallel}(\mathbf{k}, z)}, \qquad (3.16b)$$

$$S^{\perp}(\mathbf{k},z) = \frac{{}^{2}/_{3}S_{st}(\mathbf{k})}{-iz + \mathbf{k}^2 D^{\perp}(\mathbf{k}, z)}. \qquad (3.16c)$$

It should be noted that the total susceptibility should be additive [see Eq. (3.15)] and not multiplicative, as in Ref. 3.

4. EQUATION FOR THE LATERAL SELF-DIFFUSION COEFFICIENT

As pointed out above, the motion of a test chain in the lateral direction is limited by a strong mutual repulsion by the chains in the medium. In calculating the susceptibilities of a test chain and the lateral self-diffusion coefficient $D^{\perp}(\mathbf{k},z)$, we shall use the formalism of the generating functional developed in Sec. 2.

The diagram technique associated with the generating functional is analogous to that encountered in the equilibrium theory of Ref. 9, except that now the lines and vertices correspond to the relevant 2×2 matrices. This resembles the Keldysh technique for nonequilibrium systems.[17] The interaction is described by anharmonic terms of the expansion $\ln K\{\bar{\psi}_\alpha\}$ in powers of $\bar{\psi}_\alpha$. In particular, the screened intrachain interaction in the test chain is described by a fourth-order vertex. Then, applying the Dyson equation, we can write the expression for the normal component $\bar{\psi}$ correlation function in the following symbolic form:

$$\langle \psi(k)\bar{\psi}(-k)\rangle^{\perp}$$

$$= \langle \bar{\psi}(k)\bar{\psi}(-k)\rangle_0^{\perp} [1 - \Sigma(k)\langle \bar{\psi}(k)\bar{\psi}(-k)\rangle_0^{\perp}]^{-1}. \quad (4.1)$$

Here, in the Gaussian approximation the 2×2 matrix is

$$\langle \bar{\psi}_\alpha(k)\bar{\psi}_\beta(-k)\rangle_0^{\perp} = {}^{1}/_{2}U_{\alpha\tau}[1 + n^{\cdot}\hat{\Gamma}^{\perp}U]_{\tau\beta}^{-1}, \qquad (4.1a)$$

and the self-energy part in the one-loop approximation becomes

$$\Sigma_{\alpha\beta}(k) = 2n^* \int_q [\hat{\bar{\Gamma}}^{(4)}(k, q) - \hat{\Gamma}(k)\hat{\Gamma}(q)]_{\alpha\beta\omega\varkappa}$$

$$\times \langle \bar{\psi}_\omega(q)\bar{\psi}_\varkappa(-q)\rangle_0^{\perp}, \qquad (4.1b)$$

where $k = (z, \mathbf{k})$, $q = (s, \mathbf{q})$, and

$$\int_q = \int d^3q \, ds/(2\pi)^4.$$

The fourth-order vertex function $\hat{\bar{\Gamma}}^{(4)}(k, q)$ is defined by an obvious generalization of Eq. (2.8a), where following Ref. 9, we have

$$\hat{\Gamma}^{(4)}(k, q) = \hat{\Gamma}^{(4)}(q, 0, k) + \hat{\Gamma}^{(4)}(q, q + k, k)$$

$$+ \hat{\Gamma}^{(4)}(q, q + k, q)$$

$$+ \hat{\Gamma}^{(4)}(k, q + k, k) + \hat{\Gamma}^{(4)}(k, q + k, q) + \hat{\Gamma}^{(4)}(k, 0, q).$$

$$(4.2)$$

It is clear from Eq. (4.1b) that the total fourth-order vertex

$$\tilde{\Gamma}^{(4)}(k, q) = \hat{\bar{\Gamma}}^{(4)}(k, q) - \hat{\Gamma}(k)\hat{\Gamma}(q) \qquad (4.3)$$

is strongly non-Gaussian, i.e., the unconnected contributions are excluded from the vertex.

Using Eqs. (4.1) and (4.1a), as well as Eq. (2.7), we obtain the following expression for the 2×2 matrix of the $\bar{\rho}$ correlation functions

$$\langle \bar{\rho}_\alpha(k)\bar{\rho}_\beta(-k)\rangle^{\perp} = 2\{[n^{\cdot}\hat{\Gamma} - {}^{1}/_{2}\Sigma]^{-1} + U\}_{\alpha\beta}^{-1}, \qquad (4.4)$$

which yields the normal component of the correlation function of the test chain

$$G_{\alpha\beta}^{\perp}(k) = 2\hat{\Gamma}_{\alpha\beta}^{\perp}(k) - \int_q \Gamma_{\alpha\beta\omega\varkappa}^{(4)}(k, q) U_{\omega\tau}(q) [1 + n^{\cdot}\hat{\Gamma}^{\perp}(q)U(q)]_{\tau\varkappa}^{-1}.$$

$$(4.5)$$

We may conclude from Eq. (4.5) that, by analogy with the screening of the interaction in the equilibrium theory,[18] in the dynamic case the influence of the polymer medium on the test chain can be reduced to the substitution

$$U \rightarrow [U^{-1} + n^{\cdot}\hat{\Gamma}]^{-1}. \qquad (4.6)$$

However, the screening is a collective effect which occurs on a time scale considerably greater than the reptation time τ_{rept}. Figure 1 shows a series of the Edwards diagrams describing the screened interaction,[18] where the continuous lines correspond to the matrix $\hat{\Gamma}^{\perp}$ and the dashed lines to the matrix U. We can readily see that the time dependences of the terms in the series are described by the function

$$(t/\tau_{rept})^{m-1} \exp(-t/\tau_{rept}),$$

where m is the number of the continuous lines in the diagram. Therefore, if $t \ll \tau_{rept}$, we need consider only the diagram shown in Fig. 1b. In this approximation the correlation matrix of the two-component $\bar{\psi}_\alpha$ field of the medium is
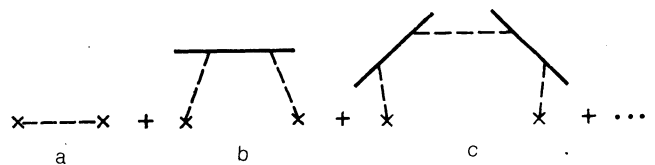

FIG. 1. Series of Edwards diagrams for the screened interaction.[18] The continuous line corresponds to the matrix $\hat{\Gamma}^{\perp}$ and the dashed line to the matrix U.

$$\mathbf{U\hat\Gamma^{\perp}U} = \begin{pmatrix} 0 & (k^2V)^2 G_{env}^{(-)} \\ (k^2V)^2 G_{env}^{(+)} & -(k^2V)^2 S_{env}^{\perp} \end{pmatrix}, \qquad (4.7)$$

where $G_{env}^{(\pm)}$ and $S_{env}^{\perp}$ are the normal components of the susceptibility and of the correlation function of the chains in the medium.

We shall now consider in greater detail the fourth-order vertex function. In the hydrodynamic approximation we can assume the vertex function to be factorized into hydrodynamic pole terms and one of the poles then applies to internal variables (which are used in the integration procedure) and the other pole to external variables. Then, elements of the total vertex, which make contribution to the convolution with the matrix of Eq. (4.7), are given by

$$\tilde\Gamma_{\psi\psi\psi\varphi}^{(4)}(k,q) = \tilde\Gamma_{\psi\psi\varphi\psi}^{(4)}(k, -q)$$

$$= \frac{[\hat{\widehat\Gamma}_{st}(\mathbf{k},\mathbf{q}) - \hat\Gamma_{st}(\mathbf{k})\,\hat\Gamma_{st}(\mathbf{q})]/T}{[-iz + \mathbf{k}^2 D^{\perp}(k)][-is + \mathbf{q}^2 D^{\perp}(q)]}, \qquad (4.8)$$

$$\tilde\Gamma_{\psi\psi\varphi\varphi}(k,q) = - \frac{\mathbf{q}^2 D^{\perp}(q)/T^2}{[-iz + \mathbf{k}^2 D^{\perp}(k)][-is + \mathbf{q}^2 D^{\perp}(q)]}$$

$$\times [\hat{\widehat\Gamma}_{st}(\mathbf{k},\mathbf{q}) - \hat\Gamma_{st}(\mathbf{k})\hat\Gamma_{st}(\mathbf{q})], \qquad (4.8a)$$

where

$$\hat{\widehat\Gamma}_{st}^{(4)}(\mathbf{k},\mathbf{q}) = \hat\Gamma_{st}^{(4)}(\mathbf{q},0,\mathbf{k}) + \hat\Gamma_{st}^{(4)}(\mathbf{q},\mathbf{q}+\mathbf{k},\mathbf{k})$$

$$+ \hat\Gamma_{st}^{(4)}(\mathbf{q},\mathbf{q}+\mathbf{k},\mathbf{q})$$

$$+ \hat\Gamma_{st}^{(4)}(\mathbf{k},\mathbf{q}+\mathbf{k},\mathbf{k}) + \hat\Gamma_{st}^{(4)}(\mathbf{k},\mathbf{q}+\mathbf{k},\mathbf{q}) + \hat\Gamma_{st}^{(4)}(\mathbf{k},0,\mathbf{q}),$$

$$(4.8b)$$

and $\hat\Gamma_{st}^{(4)}(\mathbf{q},\mathbf{p},\mathbf{k})$ is the static fourth-order density correlation function. In the case of the static second- and fourth-order correlation functions a direct calculation gives the following dependences:[9]

$$\hat\Gamma_{st}^{(4)}(\mathbf{Q}) = N^2 J(Q^2), \qquad (4.9)$$

$$\hat\Gamma_{st}^{(4)}(\mathbf{P},\mathbf{Q},\mathbf{K})$$

$$= N^4 \left[\frac{J(P^2)}{(P^2-K^2)(P^2-Q^2)} + \frac{J(Q^2)}{(Q^2-K^2)(Q^2-P^2)} + \frac{J(K^2)}{(K^2-P^2)(K^2-Q^2)} \right], \qquad (4.9a)$$

where

$$J(x) = \frac{e^{-x}-1+x}{x^2}, \qquad (4.9b)$$

$\mathbf{P} = \mathbf{p}l/(N/6)^{1/2}$, $\mathbf{Q} = \mathbf{q}l/(N/6)^{1/2}$, and $\mathbf{K} = \mathbf{k}l/(N/6)^{1/2}$.

It therefore follows that if we limit the influence of the medium on the test chain to the interaction shown in Fig. 1b, we find from Eq. (4.5) the following expression for the density correlation function of the test chain:

$$S^{\perp}(k) = 2\hat\Gamma_{00}^{\perp}(k) + \frac{n^*}{-iz + k^2 D^{\perp}(k)} \int_q [\mathbf{q}^2 V(\mathbf{q})]^2 [\hat{\widehat\Gamma}_{st}^{(4)}(\mathbf{k},\mathbf{q})$$

$$- \hat\Gamma_{st}(\mathbf{k})\,\hat\Gamma_{st}(\mathbf{q})] \left\{ \frac{G_{env}^{(+)}(q)/T}{-is + \mathbf{q}^2 D^{\perp}(q)} + \frac{G_{env}^{(-)}(q)/T}{is + \mathbf{q}^2 D^{\perp}(-q)} \right.$$

$$\left. + \frac{\mathbf{q}^2 D^{\perp}(q)\,S_{env}^{\perp}(q)/T^2}{-is + \mathbf{q}^2 D^{\perp}(q)} \right\}. \qquad (4.10)$$

We recall that the function $S^{\perp}(k)$ is given by Eq. (3.16c).

In the next section we shall show that Eq. (4.10) has a solution describing a transition of the localization–delocalization type in the case of a test chain. A similar problem for a particle diffusing in a medium of static scatterers (Lorentz model) was considered in Refs. 4 and 5. Similar problems are encountered also in the study of the diffusion of low-molecular impurities (or their self-diffusion) in a glass-forming liquid.[20,21]

5. LOCALIZATION–DELOCALIZATION TRANSITION

The localized state is usually defined in terms of fluctuation hydrodynamics as follows.[4,5,21] A mean-square displacement of a diffusing particle considered over a long time is

$$\langle r^2(t)\rangle = 6tD(z=0) + 6\frac{\partial}{\partial(-iz)}D(z)\big|_{z=0}. \qquad (5.1)$$

We can see that if

$$D(z) = (-iz)d_0^2/6, \qquad (5.2)$$

then in the limit $t \to \infty$, we have $\langle r^2(t)\rangle = d_0^2$, i.e., the state of a diffusing particle is localized and d_0 is the localization length.

A distinguishing feature of macromolecules is the fact that the localization in the lateral direction does not represent the total localization: transition takes place from the Rouse motion to reptation. For simplicity, we shall consider the case when a test chain exhibits reptation through a frozen polymer medium. We then have

$$G_{env}^{(\pm)}(q,s) = 0, \qquad S_{env}^{\perp}(q,s) = \frac{\tfrac{1}{s}\hat\Gamma_{st}(q)}{-is}. \qquad (5.3)$$

The direct correlation function corresponding to the hard-sphere potential is of the form

$$\Phi(q) = -\frac{4\pi}{q^3}(\sin \sigma q - \sigma q \cos \sigma q), \qquad (5.4)$$

where $\Phi(\mathbf{q}) = -V(\mathbf{q})/2T$ (see Sec. 2).

For convenience in further calculations we shall use the following approximations.[19] We shall represent the function (4.9b) in the form

$$J(x) \approx \frac{\tfrac{1}{2}}{1 + \tfrac{1}{2}x}, \qquad (5.5)$$

and the correlation function (4.9a) in the form

$$\hat\Gamma_{st}^{(4)}(\mathbf{P},\mathbf{Q},\mathbf{K}) \approx N^4 J(P^2) J(Q^2) J(K^2). \qquad (5.6)$$

The approximation (5.5) is valid to a high degree of precision and the expression (5.6) is satisfied approximately for pulses which are not too close to one another.

Using the approximations (5.5) and (5.6), we shall consider the vertex function in Eq. (4.10). We can see that in this case we have

$$\hat{\Gamma}^{(4)}_{st'}(\mathbf{Q},0,\mathbf{K})+\hat{\Gamma}^{(4)}_{st'}(\mathbf{K},0,\mathbf{Q})=\hat{\Gamma}_{st}(\mathbf{K})\hat{\Gamma}_{st}(\mathbf{Q}).$$

We shall assume that in Eq. (4.10) the wave vector satisfies the inequality $l^2k^2\ll 1$, so that the measured quantity is independent of details of the chemical structure of the chains. We shall consider two limits.

1. In the case of short chains $l^2k^2N\ll 1$ the greatest contribution to the vertex function comes from the term $\hat{\Gamma}^{(4)}_{st}(K,K+Q,K)$ [see Eq. (4.8b)], since the term $\hat{\Gamma}^{(4)}_{st}(\mathbf{K},\mathbf{K}+\mathbf{Q},\mathbf{Q})$, exhibits an excess negative power of a large parameter N if, for example, we integrate with respect to q. Then, using all the previous approximations in Eq. (4.10), we find that in the case of the Rouse (delocalized) motion considered in the limit of low frequencies ($z\to 0$), the diffusion coefficient is given by

$$[D^{\perp}(z=0)]^{-1}=[D_0^{\perp}]^{-1}+\frac{16c\sigma^3 N^3}{(r_g/\sigma)^4 D^{\perp}(z=0)}$$
$$\times\int_0^{\infty}dx\,\frac{x^2\left(\dfrac{\sin x}{x}-\cos x\right)^2}{[x^2+2(\sigma/r_g)^2]^2},\qquad(5.7)$$

where $D_0^{\perp}=(2/3)D_0$, $r_g^2=l^2N/6$ is the mean-square radius of inertia of a macromolecule, and c is the concentration of the segments.

The final expression for $D^{\perp}(z=0)$ in the Rouse phase is

$$D^{\perp}(z=0)={}^2\!/_3 D_0(1-N/N_c),\qquad N\leqslant N_c,\qquad(5.8)$$

where the critical chain length is defined by

$$N_c=\left(\frac{l}{2\cdot6^{1/2}\sigma}\right)^4\frac{1}{c\sigma^3}\left\{\int_0^{\infty}dx\,\frac{x^2\left(\dfrac{\sin x}{x}-\cos x\right)^2}{[x^2+2(\sigma/r_g)^2]^2}\right\}^{-1}$$
$$=\frac{1}{72}\left(\frac{l}{\sigma}\right)^4\frac{1}{cv_0}\left[1+\frac{48}{5}\left(\frac{\sigma}{l}\right)^2\frac{1}{N}+O\left(\frac{1}{N^2}\right)\right],$$
$$(5.8a)$$

and $v_0=(4/3)\pi\sigma^3$.

If $N>N_c$, then $D^{\perp}(z=0)=0$ and the lateral motion is localized. We shall seek the solution of Eq. (4.8) in the form (5.2). Then, we obtain

$$1=\frac{N}{\tilde{N}(1/N,\sigma/d_0)},\qquad(5.9)$$

where

$$\tilde{N}(1/N,\sigma/d_0)$$
$$=\left(\frac{l}{2\cdot6^{1/2}\sigma}\right)^4\frac{1}{c\sigma^3}\left\{\int_0^{\infty}dx\,\frac{x^4\left(\dfrac{\sin x}{x}-\cos x\right)^2}{[x^2+6(\sigma/d_0)^2][x^2+2(\sigma/r_g)^2]^2}\right\}^{-1}.$$
$$(5.9a)$$

At the transition point $N=N_c$ we have the real solution $\sigma/d_0=0$ and a further increase in N increases the root of the equation, i.e., the localization length d_0 disappears. Near the

transition we have $\sigma/d_0\ll 1$ and $r_g/d_0\ll 1$. Expanding the function (5.9a) near the transition apart from the first order with respect to σ/d_0, we obtain the following solution of Eq. (5.9):

$$(d_0/\sigma)^2=F(N/N_c-1)^{-1},\qquad(5.10)$$

where

$$F=6c\sigma^3\left(\frac{2\cdot6^{1/2}\sigma}{l}\right)^4\int_0^{\infty}dx\,\frac{\left(\dfrac{\sin x}{x}-\cos x\right)^2}{\left[x^2+2\left(\dfrac{\sigma}{r_g}\right)^2\right]^2}$$
$$\approx\frac{3}{10}\left(\frac{2\cdot6^{1/2}\sigma}{l}\right)^4cv_0N.\qquad(5.10a)$$

2. In the case of the opposite limit of low chains characterized by $l^2k^2N\gg 1$ (on the assumption that $l^2k^2\ll 1$) the greatest contribution to the vertex function comes from the term $\hat{\Gamma}^{(4)}_{st}(\mathbf{Q},\mathbf{K}+\mathbf{Q},\mathbf{Q})\sim K^{-2}$. We shall once again seek the solution of Eq. (4.10) in the form (5.2). Then, the equation for the square of the localization length becomes

$$1=32\cdot6^3c\sigma^3\left(\frac{\sigma}{l}\right)^6\int_0^{\infty}dx\,\frac{x^4(\sin x/x-\cos x)^2}{[x^2+6(\sigma/d_0)^2][x^2+2(\sigma/r_g)^2]^3}.$$
$$(5.11)$$

In the range under consideration we have $d_0\ll r_g$, so that in the integrand the function $1/[x^2+6(\sigma/d_0)^2]$ varies much more slowly than $1/[x^2+2(\sigma/r_g)^2]^3$. This allows us to obtain directly the solution of Eq. (5.11) in the form

$$d_0^2=l^2N_e,\qquad(5.12)$$

where

$$N_e=\frac{1}{2c\sigma^3}\left(\frac{l}{2\cdot6^{1/2}\sigma}\right)^4\left\{\int_0^{\infty}dx\,\frac{x^4\left(\dfrac{\sin x}{x}-\cos x\right)^2}{[x^2+2(\sigma/r_g)^2]^3}\right\}^{-1}$$
$$=\frac{1}{144}\left(\frac{l}{\sigma}\right)^4\frac{1}{cv_0}\left[1+\frac{72}{5}\left(\frac{\sigma}{l}\right)^2\frac{1}{N}+O\left(\frac{1}{N^2}\right)\right].$$
$$(5.12a)$$

It follows from Eq. (5.12) that the localization length d_0 plays the role of the thickness of a tube in the sense used by de Gennes,[1] where N_c is the length of a chain segment between cross-links. It is worth noting that there is also a weak dependence of N_c on N: the longer the chain, the stronger is its localization in the lateral direction. The value of N_c reaches its limit for N much greater than at the transition point. The traditional reptation model[1,2] postulates that N_c is independent of N. A more important difference is the appearance of a crystal length $N_c\approx 2N_c$ at which the localization effect begins. However, true reptatory motion occurs for much longer chain lengths when $l^2k^2N\gg 1$.

It is interesting to note that the dependence (5.12a) allows us to refine our earlier estimate of the total reptation time $\tau_{\rm rept}$. The reptation model gives the familiar estimate

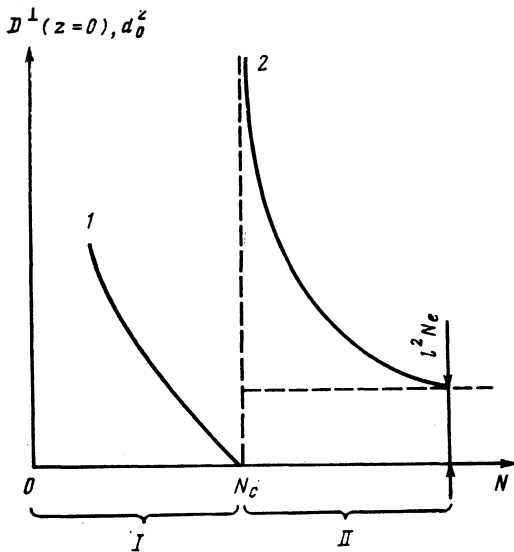$$\tau_{\rm rept}\propto\frac{N^3}{N_e}\sim N^3.\qquad(5.13)$$

FIG. 2. Schematic dependences of $D^{\perp}(z=0)$ (1) and d_0^2 (2) on the chain length N: I) Rouse phase; II) reptation phase.

In our case, instead of Eq. (5.13), we obtain

$$\tau_{\text{rept}} \propto \frac{N^3}{N_e} \propto N^3\left[1 - \frac{72}{5}\left(\frac{\sigma}{l}\right)^2 \frac{1}{N} + O\left(\frac{1}{N^2}\right)\right],$$

(5.14)

which can account fully for the experimentally observed law $\tau_{\text{rept}} \propto N^{3.4}$ (Ref. 22).

The dependence of N_c on the segment concentration c agrees with the experimental results of Ref. 22 where measurements of the compliance modulus in the high-elasticity plateau region yielded $N_c \propto c^{-1}$. The influence of the chain rigidity parameter (l/σ) is described, in accordance with Eq. (5.12a), by the law $N_c \propto (l/\sigma)^4$. An analysis of the experimental data for a large number of polymers shows that $N_c \propto l^2$ (Ref. 23). The discrepancy may be due to the fact that the result given by Eq. (5.12a) still applies to the motion of a test chain in a frozen polymer medium.

These results are shown schematically in Fig. 2. If $N < N_c$, the Rouse motion is observed. At the point $N = N_c$ a chain becomes localized in the lateral direction. Further increase in N alters the localization length d_0 which varies (as in the region of the percolation threshold) from infinity to its asymptotic value $d_0 = lN_c^{1/2}$ (when $N \to \infty$). The reptation model of Refs. 1 and 2 is valid qualitatively in this limit.

Expressions (3.15) and (3.16) representing the additivity of the density susceptibilities and correlations are defined by the self-diffusion coefficient D_s in terms of $D^{\perp}$ and $D^{\parallel}$.

In the reptation phase, we have

$$S(k,z) = \frac{a_k}{-iz} + \frac{1/3}{-iz + k^2 D^{\parallel}(k,z)},$$

(5.15)

where

$$a_k = \frac{2/3}{1 + k^2 d_0^2/6}.$$

(5.15a)

In the limit $z \to 0$ the self-diffusion coefficient is

$$\frac{1}{k^2 D_s} = \frac{a_k}{1 - a_k} \frac{1}{(-iz)} + \frac{1}{3(1-a_k)^2 k^2 D^{\parallel}}.$$

(5.16)

It follows from Eq. (5.15) that the spectrum consists of the elastic part with the Mössbauer–Lamb factor a_k and the quasielastic Lorentzian part with the width of the peak governed by the diffusion coefficient $D^{\parallel}$ of reptation.

6. CONCLUSIONS

It is shown that the polymer localization is governed by two factors: the linear connectivity of the cross-links between the macromolecules and the local anisotropy of the repulsive interaction. The linear connectivity is manifested by the fact that if some of the cross-links of a macromolecule are already localized, the others become localized more readily. This characteristic collective effect is responsible for the critical behavior of the localization length d_0 considered as a function of N (Fig. 2). However, although the transition does occur for $N = N_c$, from the experimental point of view the "strong" reptation begins only in the region where $d_0 = lN_c^{1/2}$. This can smear out greatly the transition point.

[1] P.-G. de Gennes, J. Chem. Phys. 55, 572 (1971).
[2] M. Doi and S. F. Edwards, J. Chem. Soc. Faraday Trans. II 74, 1789 (1978).
[3] W. Hess, Macromolecules 19, 1395 (1986).
[4] W. Götze, Solid State Commun. 27, 1393 (1978).
[5] W. Götze, Philos. Mag. B 43, 219 (1981).
[6] K. F. Freed, Adv. Chem. Phys. 22, 1 (1972).
[7] R. Bausch, H. K. Janssen, and H. Wagner, Z. Phys. B 24, 113 (1976).
[8] C. De Dominicis and L. Peliti, Phys. Rev. B 18, 353 (1978).
[9] T. Ohta and A. Nakanishi, J. Phys. A 16, 4155 (1983).
[10] E. A. Novikov, Zh. Eksp. Teor. Fiz. 47, 1919 (1964) [Sov. Phys. JETP 20, 1290 (1965)].
[11] M. D. Johnson, P. Hutchinson, and N. H. March, Proc. R. Soc. London Ser. A 282, 283 (1964).
[12] I. Ya. Erukhimovich and A. N. Semenov, Zh. Eksp. Teor. Fiz. 90, 259 (1986) [Sov. Phys. JETP 63, 149 (1986)].
[13] F. Brochard and P.-G. de Gennes, Physica A (Utrecht) 118, 289 (1983).
[14] A. Baumgartner and K. Binder, J. Chem. Phys. 75, 2994 (1981).
[15] K. Kremer, G. S. Grest, and I. Carmesin, Phys. Rev. Lett. 61, 566 (1988).
[16] D. Forster, Hydrodynamic Fluctuations, Broken Symmetry, and Correlation Functions, Benjamin, New York (1975).
[17] L. V. Keldysh, Zh. Eksp. Teor. Fiz. 47, 1515 (1964) [Sov. Phys. JETP 20, 1018 (1965)].
[18] S. F. Edwards, Proc. Phys. Soc. (London) 88, 265 (1966).
[19] P. Baldwin, Phys. Rev. A 34, 2234 (1986).
[20] L. Sjögren, Phys. Rev. A 33, 1254 (1986).
[21] W. Götze, Proc. NATO Advanced Study Institute on Amorphous and Liquid Materials, Passo della Mendola, Italy, 1985, publ. by Martinus Nijhoff, Dordrecht, Netherlands (1987), p. 34.
[22] W. W. Grassley, Adv. Polym. Sci. 16, 1 (1974).
[23] S. M. Aharoni, Macromolecules 16, 1722 (1983).

Translated by A. Tybulewicz