Dynamic Critical Phenomena of Polymer Solutions

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Recently, a systematic experiment measuring critical anomaly of viscosity of polymer solutions has been reported by H. Tanaka and his co-workers (Phys. Rev. E, 65, (2002), 021802). According to their experiments, the dynamic critical exponent of viscosity $y_c$ drastically decreases with increasing the molecular weight. In this article the kinetic coefficients renormalized by the non-linear hydrodynamic interaction are calculated by the mode coupling theory. We predict that the critical divergence of viscosity should be suppressed with increasing the molecular weight. The diffusion constant and the dynamic structure factor are also calculated. The present results explicitly show that the critical dynamics of polymer solutions should be affected by an extra spatio-temporal scale intrinsic to polymer solutions, and are consistent with the experiment of Tanaka, et al.

KEYWORDS: dynamic critical phenomena, model-H universality, viscoelasticity, dynamical asymmetry coupling

§1. Introduction

Dynamic critical phenomena of classical fluids have been successfully investigated by the mode coupling theory\(^1\)\(^-\)\(^3\) and the dynamic renormalization group theory.\(^4\) Because of the divergence of the correlation length $\xi$ of concentration fluctuations, the kinetic coefficients exhibit critical anomaly. According to the mode coupling theory and the dynamic renormalization group theory the anomalous kinetic coefficient for concentration behaves as $\epsilon^{-\nu x_\lambda}$,\(^3\),\(^4\) where $\nu$ is the critical exponent of $\xi$ nearly equal to 0.63 and $\epsilon = (T - T_c)/T_c$. Both theories predict that $x_\lambda \simeq 0.95$. Kawasaki\(^2\) and Perl and Ferrell\(^5\) predicted that the shear viscosity $\eta$ exhibits a logarithmic divergence:

$$\eta = \bar{\eta} \left[ 1 + \frac{8}{15\pi^2} \ln(\Lambda_0\xi) \right],$$

(1)

where $\bar{\eta}$ is the bare viscosity and $\Lambda_0$ is a microscopic cut off wave number. Later, Ohta\(^6\) pointed out that the viscosity anomaly is multiplicative and behaves as

$$\eta \sim \epsilon^{-\nu x_\eta} = \epsilon^{-y_c}.$$  

(2)
The dynamic exponent $y_c$ has a universal number about 0.04. One of the important notions in the studies of the static and dynamic critical phenomena is the universality. This insists that phenomena with the same set of critical exponents form a universality class. Dynamic critical phenomena of classical fluids belong to the model $H$ universality in the Hohenberg-Halperin classification.

It has been believed that the critical dynamics of complex fluids such as polymer solutions also belongs to the model $H$ universality. Contrary to this conventional understanding, some experimental works have questioned that the dynamic critical phenomena of polymer solutions can be really categorized into the model $H$ universality. In fact the dynamic exponent $y_c$ obtained experimentally for polymer solutions is smaller than that in classical fluids. Recently H. Tanaka and his co-workers have reported experimental work of dynamic critical phenomena of polymer solutions. Their accurate measurements for critical anomaly of viscosity show that the dynamic exponent $y_c$ significantly decreases as the molecular weight $M_w$ increases. That is, in polymer solutions with large molecular weight the critical divergence of viscosity is suppressed. They also measured the dynamic structure factor by the light scattering experiment. It has been found that in the case of large molecular weight the dynamic structure factor cannot be expressed by the Kawasaki scaling function even in the vicinity of the critical point. On the basis of such experimental facts, they concluded that the critical dynamics of polymer solutions exhibits a non-universal nature and cannot be classified into the model $H$ universality in a practical sense. They supposed that such a nontrivial behavior is due to the dynamic coupling between critical concentration fluctuations and another slow viscoelastic mode which is intrinsic to polymer solutions. It should be noted that the viscoelastic effect and the break-down of the model $H$ universality have been definitely confirmed in the studies for the phase separations of polymer solutions and dynamically asymmetric polymer blends.

Motivated by the experiments reported by Tanaka, et al., we shall investigate the dynamic critical phenomena of polymer solutions by the mode coupling theory. In the present analysis we use the two-fluid model as the basic equations describing the dynamics of polymer solutions. The two-fluid model was put forward by Brochard and de Gennes. Later, the current form of the two-fluid model was derived by Doi and Onuki. It has been successfully used to explain various phenomena such as shear induced concentration fluctuations, non-exponential decay in dynamic scattering near equilibrium, phase separation dynamics, and so on. However, the critical anomaly of polymer solutions has not been studied by the two-fluid model.

Although the viscoelastic effect on the relaxation of the concentration fluctuations have been studied by a number of people within the framework of the two-fluid model (see for example ref. 19), the past studies were mainly performed in the systems where the mode coupling is not effective on the thermal relaxations, such as one phase region far from the critical point, very
viscous polymer solutions and polymer blends, and so on. Therefore, in these analyses the velocity fluctuations have not been explicitly taken into consideration. Consequently, they neglected the effect of the mode coupling on the thermal decay rates. However, near the critical point in the semi-dilute polymer solutions, the dynamics of the critical fluctuations is strongly influenced by the non-linear hydrodynamic interaction arising from the streaming type mode coupling. As a result, the kinetic coefficients, observed near the critical point, are renormalized by the non-linear hydrodynamic interaction. In the present analysis such a non-linear hydrodynamic interaction is successfully taken into account by the mode coupling theory. We then show that the viscoelasticity affects the critical dynamics of polymer solutions, resulting in a suppression of the divergence of viscosity. This result properly explains the experiments reported by Tanaka, et al.

The organization of the present paper is as follows: In §2 we briefly review the two-fluid model for the polymer solutions. In §3 we analyze the viscoelastic effect on the relaxation of the concentration fluctuations and the velocity fluctuations within the linearized two-fluid model equations and derive the bare (unperturbed) propagators which give a starting point of the mode coupling analysis performed in §4. Here we shall evaluate the complex shear viscosity that is non-local both in space and time, which results from the dynamical asymmetry coupling between the viscoelastic stress and the velocity fluctuations. In §4 we investigate the critical anomaly, constructing self-consistent equations for the propagators by means of the mode coupling theory. The kinetic coefficients renormalized by the non-linear hydrodynamic interaction which is important in the vicinity of the critical point are calculated. In the final section we will give some remarks about the present analysis.

§2. Basic equations

In this article we use the two-fluid model for the basic equations to describe the dynamics of polymer solutions. Here we briefly survey the two-fluid model equations. The readers who want to know the details of the two-fluid model, see the original paper or excellent reviews.

Let $v_p(r,t)$ and $v_s(r,t)$ be the average velocities of polymer and solvent, respectively, and $\psi(r,t)$ is the volume fraction of polymer at point $r$ and time $t$. We assume that the solution is incompressible and that polymer and solvent have the same specific volume. Thus $\psi$ satisfies a conservation law with $v_p$:

$$\frac{\partial \psi}{\partial t} = -\nabla \cdot (\psi v_p). \quad (3)$$

The volume-averaged velocity $v = \psi v_p + (1 - \psi) v_s$ obeys the following hydrodynamic equation

$$\rho \frac{\partial v}{\partial t} = -\nabla p + \eta_0 \nabla^2 v - \psi \nabla \frac{\delta F}{\delta \psi} + \nabla \cdot \sigma^p. \quad (4)$$

where $\rho$ is the average mass density, $\eta_0$ is the solvent viscosity, $F$ is the free energy functional of the system, and $\sigma^p$ is the viscoelastic stress. The hydrostatic pressure $p$ is determined by the
incompressibility condition
\[ \nabla \cdot \mathbf{v} = 0. \]  

(5)

For slow motions, the two-fluid model gives the convective velocity of polymer \( \mathbf{v}_p \) as

\[ \mathbf{v}_p = \mathbf{v} + \frac{(1 - \psi)^2}{\zeta(\psi)} \left( -\psi \nabla \frac{\delta F}{\delta \psi} + \nabla \cdot \hat{\sigma}_p \right), \]  

(6)

where \( \zeta(\psi) \) is the friction coefficient between the two components, and is given by

\[ \zeta(\psi) = 6\pi \eta_0 \xi_b^{-2}. \]  

(7)

Here \( \xi_b \) is the blob length of order \( b/\psi \), with \( b \) being the monomer size. Eqs. (3) and (6) imply that the non-vanishing viscoelastic stress produces a diffusion. This effect is called the stress-diffusion coupling. The viscoelastic stress due to the network deformations is given by

\[ \hat{\sigma}_p = G(\psi) \hat{W} \cdot (\hat{W} - \hat{\delta}). \]  

(8)

This form is derived from the free energy functional introduced in eq.(10) shown below. Here \( G(\psi) \) is the \( \psi \)-dependent shear modulus, \( \hat{\delta} \) denotes the unit matrix and \( \hat{W} \) is interpreted as a long lived strain variable. We assume that the equation of motion of \( \hat{W} \) is given by the following dynamic equation,\(^{25, 26}\)

\[ \frac{\partial \hat{W}}{\partial t} + (\mathbf{v}_p \cdot \nabla) \hat{W} = (\nabla \mathbf{v}_p^T \cdot \hat{W} + \hat{W} \cdot \nabla \mathbf{v}_p) - \frac{1}{\tau}(\hat{W} - \hat{\delta}), \]  

(9)

where \( \tau(\psi) \) is the \( \psi \)-dependent relaxation time of shear stress.

\section*{3. Linear Response}

In this section we examine the effect of the viscoelasticity on the relaxation of the concentration fluctuations and the velocity fluctuations, based on the linearized two-fluid model equations. We then obtain the bare (unperturbed) propagators which give the starting point of the mode coupling analysis performed in the next section. Previously, Doi and Onuki\(^{19}\) showed that the diffusion process is drastically influenced by the dynamical asymmetry coupling (\( \alpha \neq 0 \)) between the concentration fluctuations and the longitudinal mode of the viscoelastic force (stress-diffusion coupling). Their analysis predicted an additional wave number dependence of the diffusion coefficient due to the viscoelasticity, which was confirmed by the recent experimental studies (see for example ref. 27). However, in their analysis the very viscous systems without the velocity fluctuations were assumed, so the effect of the viscoelasticity on the relaxation of the velocity fluctuations (hydrodynamic relaxation) was not investigated. Here we take the transverse parts of the viscoelastic force and the velocity fluctuations into consideration. We shall then show that the dynamical asymmetry coupling between these transverse modes has a strong influence on the hydrodynamic relaxation, resulting in a wave number dependent shear viscosity.
The relaxation dynamics of the thermal fluctuations in a one phase region far from the critical point is still described by the linearized equations. Since the longitudinal modes do not couple to the transverse modes within the linearized equations, the diffusion process far from the critical point should not be influenced by the hydrodynamic relaxation. However, the situation is completely different in the vicinity of the critical point, since the non-linear hydrodynamic interaction, resulting from the streaming type mode coupling, becomes dominant. In the next section this will be shown by means of the mode coupling theory.

Now we shall investigate the relaxation dynamics of concentration fluctuations and velocity fluctuations within the linearized approximation of the set of equations represented in §2. We set \( \tau_0 = \tau(\psi_0) \) and \( G_0 = G(\psi_0) \) with \( \psi_0 \) being the average concentration. The free energy functional is assumed to be of the following Ginzburg-Landau type

\[
F\{\psi, \hat{W}\} = \int d\mathbf{r} \left[ \frac{1}{2} r_0 \psi^2 + \frac{1}{2} c_0 |\nabla \psi|^2 + \frac{1}{4} G_0 \delta W_{ij}^2 \right],
\]

where \( \delta W_{ij} = W_{ij} - \delta_{ij} \). The Fourier transform of an arbitrary function \( g(\mathbf{r}) \) is defined by

\[
g_k = \int d\mathbf{r} e^{-i\mathbf{k}\cdot\mathbf{r}} g(\mathbf{r}).
\]

In terms of the Fourier components, the linearized equations are given by

\[
\rho \frac{\partial \mathbf{v}_k^\perp}{\partial t} = -\eta_0 k^2 \mathbf{v}_k^\perp + i(\hat{\delta} - \hat{\mathbf{k}}) \cdot \mathbf{k} \cdot \hat{\sigma}_k^p,
\]

\[
\frac{\partial}{\partial t} \delta \psi_k = -\Gamma_k \delta \psi_k + \alpha L \mathbf{k} \cdot \hat{\sigma}_k^p,
\]

\[
\frac{\partial}{\partial t} \sigma_{k,ij}^p = -\frac{1}{\tau_0} \sigma_{k,ij} + i G_0 (k_i v_k^\perp + k_j v_{k,ji})
+ 2G_0 \alpha \Gamma_k \hat{k}_i \hat{k}_j \delta \psi_k - G_0 \alpha^2 L k^2 (\hat{k}_i \hat{k}_j \sigma_{k,ij}^p + \hat{k}_j \hat{k}_i \sigma_{k,ji}^p),
\]

\[
\sigma_{k,ij}^p = G_0 \delta W_{k,ij},
\]

where \( \mathbf{v}_k^\perp \) is the transverse part of \( \mathbf{v}_k \), \( \hat{\mathbf{k}} = \mathbf{k}/k \), and

\[
\alpha = \frac{1}{\psi_0}
\]

is the dynamical asymmetry parameter of the polymer solutions. The kinetic coefficient \( L \) is given by

\[
L = \psi_0^2 (1 - \psi_0)^2 / \zeta(\psi_0).
\]

The decay rate in the absence of the viscoelastic coupling is given by

\[
\Gamma_k = L (r_0 + c_0 k^2) k^2.
\]

Here and in the following the Einstein summation convention has been adopted. The viscoelastic force \( \mathbf{f} \) is defined as follows:

\[
\mathbf{f} \equiv \nabla \cdot \hat{\sigma}_p.
\]
For the present purpose it is convenient to decompose the Fourier transform $f_k$ of the viscoelastic force into the longitudinal and the transverse components,

$$f_k = \hat{k} \cdot f_k + (\delta - \hat{k}) \cdot f_k.$$  \hspace{1cm} (20)

Let us set

$$f_k^\parallel \equiv \hat{k} \cdot f_k,$$  \hspace{1cm} (21)

$$f_k^\perp \equiv (\delta - \hat{k}) \cdot f_k.$$  \hspace{1cm} (22)

From the linearized equations (12)-(15), we obtain the following two sets of equations of motion for the longitudinal modes and the transverse modes.

For the longitudinal modes, we obtain

$$\frac{\partial}{\partial t} \delta \psi_k = -\Gamma_k \delta \psi_k - \alpha L Z_k + R^\psi_k(t),$$  \hspace{1cm} (23)

$$\frac{\partial}{\partial t} Z_k = -\frac{1}{\tau_0} (1 + 2\xi_{ve}^2 k^2) Z_k - 2G_0 \alpha \Gamma_k \delta \psi_k + R^Z_k(t),$$  \hspace{1cm} (24)

where $Z_k = i k \cdot f_k^\parallel$ and $\xi_{ve}$ is a viscoelastic length or a magic length defined by

$$\xi_{ve} \equiv \sqrt{G_0 \tau_0 \alpha^2 L}.$$  \hspace{1cm} (25)

This length was first introduced by Brochard and de Gennes.\textsuperscript{17,18} The physical significance of the viscoelastic length has been discussed by many researchers (see for example refs. 16 and 26).

For the transverse modes, we obtain

$$\frac{\partial v_k^\perp}{\partial t} = -\eta_0 k^2 \psi_k + \frac{1}{\rho} f_k^\perp + R^\psi_k(t),$$  \hspace{1cm} (26)

$$\frac{\partial f_k^\perp}{\partial t} = -\frac{1}{\tau_0} (1 + 2\xi_{ve}^2 k^2) f_k^\perp - G_0 k^2 \psi_k + R^f_k(t).$$  \hspace{1cm} (27)

Here $R^\psi_k, R^Z_k, R^\psi_k$ and $R^f_k$ are random forces.

First we formally solve eqs. (23) and (24) as

$$\delta \psi_k(t) = G^{\psi \psi}_k(t) \delta \psi_k(0) + G^{\psi Z}_k(t) Z_k(0)$$

$$+ \int_0^t ds G^{\psi \psi}_k(t-s) R^\psi_k(s) + \int_0^t ds G^{\psi Z}_k(t-s) R^Z_k(s),$$  \hspace{1cm} (28)

$$Z_k(t) = G^{Z \psi}_k(t) \delta \psi_k(0) + G^{ZZ}_k(t) Z_k(0)$$

$$+ \int_0^t ds G^{Z \psi}_k(t-s) R^\psi_k(s) + \int_0^t ds G^{ZZ}_k(t-s) R^Z_k(s),$$  \hspace{1cm} (29)

where the propagators $G(t)$'s are written as

$$G^{\psi \psi}_k(t) = \frac{1}{\omega_+ - \omega_-} \left\{ \left[ \omega_+ - \frac{1}{\tau_0} (1 + 2\xi_{ve}^2 k^2) \right] \exp(-\omega_+ t) + \left[ -\omega_- + \frac{1}{\tau_0} (1 + 2\xi_{ve}^2 k^2) \right] \exp(-\omega_- t) \right\},$$
The propagator $G^\psi(t)$ is the dynamic structure factor, and it is expressed by a superposition of two exponential functions. This form of the dynamic structure factor was first proposed by Brochard and de Gennes\(^\text{17,18}\) on the basis of a phenomenological argument. Afterwards, Doi and Onuki\(^\text{19}\) derived the same form of the structure factor by analysing their two-fluid model equations which is employed in the present analysis (see also ref. 24).

Similarly as above, we can formally solve eqs. (26) and (27) and obtain

\[
G^\psi(t) = \frac{\alpha L}{\omega_+ - \omega_-} \left[ \exp(-\omega_+ t) - \exp(-\omega_- t) \right],
\]

\[
G^Z(t) = \frac{2G_0\alpha \Gamma_k k^2}{\omega_+ - \omega_-} \left[ \exp(-\omega_+ t) - \exp(-\omega_- t) \right],
\]

\[
G^{ZZ}(t) = \frac{1}{\omega_+ - \omega_-} \left[ (\omega_+ - \Gamma_k) \exp(-\omega_+ t) + (-\omega_- + \Gamma_k) \exp(-\omega_- t) \right].
\]

The relaxation rates, $\omega_+$ and $\omega_-$ are given by

\[
\omega_\pm = \frac{1}{2} \left\{ \left[ \Gamma_k + \frac{1}{\tau_0} (1 + 2\xi_{ve} k^2) \right] \pm \sqrt{\left[ \Gamma_k + \frac{1}{\tau_0} (1 + 2\xi_{ve} k^2) \right]^2 - 4 \Gamma_k \frac{\tau_0}{G_0}} \right\}.
\]

The propagator $G^\psi(t)$ is the dynamic structure factor, and it is expressed by a superposition of two exponential functions. This form of the dynamic structure factor was first proposed by Brochard and de Gennes\(^\text{17,18}\) on the basis of a phenomenological argument. Afterwards, Doi and Onuki\(^\text{19}\) derived the same form of the structure factor by analysing their two-fluid model equations which is employed in the present analysis (see also ref. 24).

Similarly as above, we can formally solve eqs. (26) and (27) and obtain

\[
\mathbf{v}^\perp_k(t) = H^\perp_k(t) \mathbf{v}^\perp_k(0) + H^\perp_k(t) \mathbf{f}^\perp_k(0)
\]

\[
+ \int_0^t ds H^\perp_k(t-s) \mathbf{R}^\perp_k(s) + \int_0^t ds H^\perp_k(t-s) \mathbf{R}^\perp_k(s),
\]

\[
f^\perp_k(t) = H^\perp_k(t) \mathbf{v}^\perp_k(0) + H^\perp_k(t) \mathbf{f}^\perp_k(0)
\]

\[
+ \int_0^t ds H^\perp_k(t-s) \mathbf{R}^\perp_k(s) + \int_0^t ds H^\perp_k(t-s) \mathbf{R}^\perp_k(s).
\]

where the propagators $H(t)$'s are given by

\[
H^\perp_k(t) = \frac{1}{\Omega_+ - \Omega_-} \left\{ \left[ \Omega_+ - \frac{1}{\tau_0} (1 + \xi^2_{ve} k^2) \right] \exp(-\Omega_+ t) + \left[ -\Omega_- + \frac{1}{\tau_0} (1 + \xi^2_{ve} k^2) \right] \exp(-\Omega_- t) \right\},
\]

\[
H^\perp_k(t) = -\frac{\rho^{-1}}{\Omega_+ - \Omega_-} \left[ \exp(-\Omega_+ t) - \exp(-\Omega_- t) \right],
\]

\[
H^\perp_k(t) = \frac{G_0 k^2}{\Omega_+ - \Omega_-} \left[ \exp(-\Omega_+ t) - \exp(-\Omega_- t) \right],
\]

\[
H^\perp_k(t) = \frac{1}{\Omega_+ - \Omega_-} \left[ \left( \Omega_+ - \frac{\eta_0 k^2}{\rho} \right) \exp(-\Omega_+ t) + \left( -\Omega_- + \frac{\eta_0 k^2}{\rho} \right) \exp(-\Omega_- t) \right].
\]

The relaxation rates $\Omega_+$ and $\Omega_-$ are given by

\[
\Omega_\pm = \frac{1}{2} \left\{ \left[ \frac{\eta_0 k^2}{\rho} + \frac{1}{\tau_0} (1 + \xi^2_{ve} k^2) \right] \pm \sqrt{\left[ \frac{\eta_0 k^2}{\rho} - \frac{1}{\tau_0} (1 + \xi^2_{ve} k^2) \right]^2 - 4 G_0 k^2} \right\}.
\]
The viscoelasticity is characterized by the complex shear modulus \( G^*_k(\omega) = G'_k(\omega) + iG''_k(\omega) \), where \( G'_k(\omega) \) and \( G''_k(\omega) \) are called the storage modulus and the loss modulus, respectively.\(^{31}\)

From the Eqs.(26) and (27), the total shear stress \( \hat{\sigma}_k(\omega) \) is expressed as

\[
\sigma_{k,ij}(\omega) = \frac{G^*_k(\omega)}{i\omega} [ik_i v^x_{k,j}(\omega) + ik_j v^x_{k,i}(\omega)],
\]

where we have introduced the Laplace transforms of \( v^x_k(t) \) and \( \hat{\sigma}_k(t) \) as

\[
v^x_k(\omega) = \int_0^\infty dt v^x_k(t)e^{-i\omega t},
\]

\[
\hat{\sigma}_k(\omega) = \int_0^\infty dt \hat{\sigma}_k(t)e^{-i\omega t}.
\]

In the present system \( G'_k(\omega) \) and \( G''_k(\omega) \) are given by

\[
G'_k(\omega) = \frac{G_0^2 \omega^2}{\omega^2 \tau_0^2 + (1 + \xi_{ve}^2 k^2)^2},
\]

\[
G''_k(\omega) = \omega \left[ \eta_0 + G_0 \tau_0 \frac{1 + \xi_{ve}^2 k^2}{\omega^2 \tau_0^2 + (1 + \xi_{ve}^2 k^2)^2} \right],
\]

which are non-local both in space and time. The complex shear viscosity is given by

\[
\eta_k(\omega) = \frac{G^*_k(\omega)}{i\omega}.
\]

The imaginary part of \( G^*_k(\omega) \) gives the shear viscosity for long time scale motion (\( \omega \approx 0 \)) as

\[
\eta_k(0) = \lim_{\omega \to 0} \frac{G''_k(\omega)}{\omega} = \eta_0 + \eta_p \frac{1}{1 + \xi_{ve}^2 k^2},
\]

where we have defined \( \eta_p \equiv G_0 \tau_0 \). The asymptotic behavior of \( \eta_k(0) \) is represented by

\[
\eta_k(0) \cong \eta_0 + \eta_p \quad (k \xi_{ve} \ll 1),
\]

\[
\cong \eta_0 + \eta_p \frac{1}{\xi_{ve}^2 k^2} \quad (k \xi_{ve} \gg 1).
\]

For polymer solutions the two-fluid model gives the viscoelastic length as\(^{19,26}\)

\[
\xi_{ve} \cong (\eta_p/\eta_0)^{\frac{1}{2}} \xi_b.
\]

Thus, Eq.(50) is also expressed as

\[
\eta_k(0) \cong \eta_0 \left( 1 + \frac{1}{\xi_b^2 k^2} \right), \quad (k \xi_{ve} \gg 1),
\]

which explicitly shows that the hydrodynamic interaction becomes weak beyond the blob length \( \xi_b \). It is worth mentioning that this property is due to the dynamical asymmetry coupling (\( \alpha \neq 0 \)) between the viscoelastic stress and the velocity fluctuations. For polymer solutions, it is well known that the diffusion process is drastically influenced by the dynamical asymmetry coupling between the longitudinal modes, namely the so-called stress-diffusion coupling.\(^{17–19}\) The present analysis shows that the dynamical asymmetry coupling between the transverse modes is also important for the hydrodynamic relaxation process.
§4. Mode coupling approach

In this section we discuss the critical anomaly of the kinetic coefficients. If we take the whole non-linearity into consideration, many terms appear even in the second order in the perturbation expansion in terms of fluctuations and the analytical approach becomes very complicated. However, it turns out that there are only a few non-linear terms which crucially affect the critical dynamics. From the equations of motion represented in §2, we find that the non-linear terms, associated with the viscoelasticity, are so much smaller than the linear terms which are represented in the linearized equations (12)-(15) that we may safely discard the non-linear terms arising from the viscoelasticity, and retain only two streaming type mode coupling terms which arise from the hydrodynamic interaction: One is the convection term of $v$ in the equation for $\psi$ and the other is the osmotic pressure gradient term in the hydrodynamic equation. We consider these nonlinearity up to the second order of the perturbation expansion. As a result the equations of motion that we must analyze are given as follows:

$$
\rho \frac{\partial v_k^\perp}{\partial t} = -\eta_0 k^2 v_k^\perp + i(\delta - \hat{k}\hat{k}) \cdot [k \cdot \hat{\sigma}_k^p - \int_p \{r_0 + c_0 p^2\} \psi_{k-p} \psi_p],
$$

$$
\frac{\partial}{\partial t} \delta \psi_k = -\Gamma_k \delta \psi_k + \alpha L k \cdot k \cdot \hat{\sigma}_k^p - \hat{k} \cdot \int_p \psi_p v_k^\perp,
$$

$$
\frac{\partial}{\partial t} \sigma_{k,ij}^p = - \frac{1}{\tau_0} \sigma_{k,ij}^p + iG_0(k_i v_{k,j}^\perp + k_j v_{k,i}^\perp)
+ 2G_0\alpha \Gamma_k \hat{k}_i \hat{k}_j \delta \psi_k - G_0 \alpha^2 L k^2(\hat{k}_i \hat{k}_j \sigma_{k,ij}^p + \hat{k}_j \hat{k}_j \sigma_{k,ji}^p),
$$

As shown in the following sub-sections, our analysis based on the above set of equations well explains the experimental results.\(^{15}\)

4.1 Self-consistent Equations for Propagators

In this sub-section we construct the self-consistent equations for the propagators within the mode coupling theory.\(^{1,2}\) By the simplest approximation we obtain the following set of self-consistent equations for the propagators:

$$
\frac{\partial}{\partial t} \hat{G}_k(t) = -\hat{L}_k^G \cdot \hat{G}_k(t)
- k_B T \rho \int_0^t \rho \int_p \{1 - (\hat{p} \cdot \hat{k})^2\} \frac{\langle |\psi_k - p| \rangle^2}{\langle |\psi_k| \rangle^2} H_{p}^{\psi\psi}(s) G_{k-p}^{\psi\psi}(s) \hat{E} \cdot \hat{G}_k(t-s),
$$

$$
\frac{\partial}{\partial t} \hat{H}_k(t) = -\hat{L}_k^H \cdot \hat{H}_k(t)
- k_B T \rho \int_0^t \rho \int_p \{1 - (\hat{p} \cdot \hat{k})^2\} \times
\langle |\psi_k - p| \rangle^2 \langle |\psi_p| \rangle^2 \frac{1}{\langle |\psi_p| \rangle^2} - \frac{1}{\langle |\psi_k - p| \rangle^2} \rangle^2 G_p^{\psi\psi}(s) G_{k-p}^{\psi\psi}(s) \hat{E} \cdot \hat{H}_k(t-s),
$$

9
where \( \langle \cdots \rangle \) denotes the equilibrium average,

\[
\hat{L}_G^k = \left( \begin{array}{cc} L_{\psi \psi}^k & L_{\psi Z}^k \\ L_{Z \psi}^k & L_{Z Z}^k \end{array} \right) = \left( \begin{array}{cc} \Gamma_k & \frac{\alpha L}{2G_0\alpha \kappa^2_k} \\ \frac{1}{\tau_0} (1 + 2\xi^2_{\nu} k^2) & -\frac{1}{\rho} \end{array} \right),
\]

(59)

\[
\hat{L}_H^k = \left( \begin{array}{cc} L_{\nu \nu}^k & L_{\nu f}^k \\ L_{f \nu}^k & L_{f f}^k \end{array} \right) = \left( \begin{array}{cc} \frac{\eta_0}{\rho} \kappa^2_k & \frac{-1}{\rho} \\ \frac{\rho - 1}{\rho} \kappa^2_k & \frac{1}{\tau_0} (1 + \xi^2_{\nu} k^2) \end{array} \right),
\]

(60)

and the matrix \( \hat{E} \) is given by

\[
\hat{E} = \left( \begin{array}{ccc} 1 & 0 & 0 \\
0 & 0 & 0 \end{array} \right).
\]

(61)

Equations (57) and (58) correspond to the diagrammatic one-loop approximation, neglecting vertex corrections.

### 4.2 Renormalized Diffusion Constant

First we calculate the diffusion constant and the dynamic structure factor in the vicinity of the critical point. The equations for the propagators can be written as

\[
\left[ i\omega \hat{\delta} + \hat{L}_G^k + \Sigma_G^k(\omega) \hat{E} \right] \cdot \hat{G}_k(\omega) = \hat{\delta},
\]

(62)

\[
\left[ i\omega \hat{\delta} + \hat{L}_H^k + \Sigma_H^k(\omega) \hat{E} \right] \cdot \hat{H}_k(\omega) = \hat{\delta},
\]

(63)

where

\[
\dot{G}_k(\omega) = \int_0^\infty dt e^{-i\omega t} G_k(t),
\]

(64)

\[
\dot{H}_k(\omega) = \int_0^\infty dt e^{-i\omega t} H_k(t).
\]

(65)

Here the self-energies \( \Sigma_G^k(\omega) \) and \( \Sigma_H^k(\omega) \) are given by

\[
\Sigma_G^k(\omega) = \frac{k_B T}{\rho} \int_0^\infty ds \int_p k^2 [1 - (\hat{p} \cdot \hat{k})^2] \frac{\langle |\psi_{k-p}^\psi|^2 \rangle}{\langle |\psi_k^\psi|^2 \rangle} H_p^{\nu \nu}(s) G_{k-p}^{\psi \psi}(s) e^{-i\omega s},
\]

(66)

\[
\Sigma_H^k(\omega) = \frac{k_B T}{4\rho} \int_0^\infty ds \int_p \rho^2 [1 - (\hat{p} \cdot \hat{k})^2] \times \langle |\psi_{k-p}^\psi|^2 \rangle \langle |\psi_p^\psi|^2 \rangle (\frac{1}{\langle |\psi_p^\psi|^2 \rangle} - \frac{1}{\langle |\psi_{k-p}^\psi|^2 \rangle})^2 G_p^{\psi \psi}(s) G_{k-p}^{\psi \psi}(s) e^{-i\omega s}.
\]

(67)

These equations are so complicated that it is hopeless to solve them analytically in general situations. However, near the critical point we are allowed to investigate eqs. (66) and (67) by the following iterative manner.

First we evaluate \( \Sigma_G^k(\omega) \) assuming that the shear viscosity does not exhibit any critical anomaly. As we shall see in the following analysis, the decay of \( G_{k-p}^{\psi \psi}(t) \) is governed by the slowest mode near the critical point. Therefore, \( H_p^{\nu \nu}(s) \) in (66) is given by (37), so that we may set \( G_{k-p}^{\psi \psi}(s) \approx 1 \).

Considering the decay of concentration fluctuation, \( \omega \) in (66) is much smaller than \( \Omega_+ \) or \( \Omega_- \),
where we use the Markov approximation to set $\omega = 0$ in (66). That is, our present analysis can be regarded as the zeroth order approximation for the additional frequency dependencies of the decay rates. If we use the Ornstein-Zernike form for $|\psi_k|^2 \propto (k^2 + \xi^{-2})^{-1}$, the resultant equations can be integrated appropriately as follows:

\[
\Sigma_k^G(0) \approx \int \frac{k_B T k^2}{p^2} \left[ 1 - (\hat{k} \cdot \hat{p})^2 \right] \frac{1 + \xi_{ve}^2 p^2}{\eta_0 + \eta_p + \eta_0 \xi_{ve}^2 p^2} \frac{1 + \xi^2 k^2}{1 + \xi^2 (k - \hat{p})^2} \\
= \int \frac{k_B T k^2}{p^2} \left[ 1 - (\hat{k} \cdot \hat{p})^2 \right] \frac{1 + \xi^2 k^2}{1 + \xi^2 (k - \hat{p})^2} + \int \frac{k_B T k^2}{p^2} \left[ 1 - (\hat{k} \cdot \hat{p})^2 \right] \frac{\eta_p \xi_{ve}^2 p^2}{\eta_0 + \eta_p + \eta_0 \xi_{ve}^2 p^2} \frac{1 + \xi^2 k^2}{1 + \xi^2 (k - \hat{p})^2} \\
= \frac{k_B T}{6\pi(\eta_0 + \eta_p)\xi^3} \left[ K(x) + \frac{\eta_p}{\eta_0} F(x, A) \right],
\]

where $x = \xi k$, $k_B$ is the Boltzmann constant, and the parameter $A$ is given by

\[
A = \frac{\xi}{\xi_{ve} \sqrt{1 + \frac{\eta_p}{\eta_0}}}. 
\]

By using eq.(51), in the case $\eta_p \gg \eta_0$ $A$ is practically the ratio of the correlation length $\xi$ to the blob length $\xi_b$

\[
A \approx \frac{\xi}{\xi_b}. 
\]

In eq.(68) the first term is the Kawasaki scaling function, given by

\[
K(x) = \frac{3}{4} \left[ 1 + x^2 + (x^3 - x^{-1}) \tan^{-1} x \right].
\]

In the present case an additional term $F(x, A)$ arises from the viscoelasticity, which is given by

\[
F(x, A) = \frac{3}{4} x^2 (1 + x^2) \left\{ \frac{1}{2x^2} \left( 1 + \frac{1 + x^2 - A^2}{A} \right) + \left[ \frac{x^2 - 1}{2x^3} - \frac{(1 + x^2)^2 - A^4}{4A^2 x^3} \right] \tan^{-1} x \right. \\
\left. - \frac{1 + x^2 - A^2}{2Ax^2} \left[ 1 + \frac{(1 + x^2 - A^2)^2}{4A^2 x^2} \right] \frac{2Ax}{1 + x^2 - A^2} \tan^{-1} \left( \frac{2Ax}{1 + x^2 - A^2} \right) \right\},
\]

where

\[
s = \frac{(1 + x^2 - A^2)^2}{4A^2 (1 + x^2)}. 
\]

Though the above expression is very complicated, its asymptotic form becomes simpler:

\[
\Sigma_k^G(0) \approx \frac{k_B T}{6\pi \xi^3 (\eta_0 + \eta_p)} x^2 \left( 1 + \frac{\eta_p}{\eta_0 A} \right), \quad (k \ll \frac{1}{\xi}),
\]

\[
(74)
\]

11
\[ \approx \frac{k_B T}{16\xi^3(\eta_0 + \eta_p)} x^3 \left( 1 + \frac{8\eta_p}{3\pi\eta_0 A} x \right), \quad \left( \frac{1}{\xi} \ll k \ll \frac{1}{\xi_b} \right), \tag{75} \]
\[ \approx \frac{k_B T}{16\xi^3\eta_0} x^3, \quad (k \gg \frac{1}{\xi_b}). \tag{76} \]

Here we have neglected the terms irrelevant to the following analysis. We plot the reduced self energy and its asymptotic form for various values of \( \eta_p/\eta_0 \) and \( A \) in Figs. 1(a)-(f). We note that the dynamic scaling is violated and the self energy cannot be expressed by the Kawasaki scaling function. This is evident from Fig. 1(a) and Fig. 1(d) where the viscoelasticity is found to be relatively strong.

The dynamic structure factor is given by
\[
G^{\psi\psi}_k(t) = \frac{1}{\bar{\omega}_+ - \bar{\omega}_-} \left\{ \left[ \bar{\omega}_+ - \frac{1}{\tau_0} (1 + 2\xi^2_{ve} k^2) \right] \exp(-\bar{\omega}_+ t) + \left[ -\bar{\omega}_- + \frac{1}{\tau_0} (1 + 2\xi^2_{ve} k^2) \right] \exp(-\bar{\omega}_- t) \right\},
\tag{77}
\]
where the renormalized relaxation rates, \( \bar{\omega}_+ \) and \( \bar{\omega}_- \) are obtained as
\[ \bar{\omega}_\pm = \frac{1}{2} \left\{ \Gamma_k + \Sigma^G_k(0) + \frac{1}{\tau_0} (1 + 2\xi^2_{ve} k^2) \right\} \pm \frac{1}{2} \left\{ \Gamma_k + \Sigma^G_k(0) + \frac{1}{\tau_0} (1 + 2\xi^2_{ve} k^2) \right\} \frac{1}{4\tau_0} \left[ \Gamma_k + \Sigma^G_k(0) (1 + 2\xi^2_{ve} k^2) \right] \}. \tag{78} \]

A comment will be made on the above results. Although the functional form of the dynamic structure factor \( G^{\psi\psi}_k(t) \) is the same as eq.(30) derived in the previous section, the relaxation rates \( \bar{\omega}_k \) of the critical concentration fluctuations obtained here are the ones renormalized by the non-linear hydrodynamic interaction.

In the vicinity of the critical point \( \Sigma^G_k(0) \) dominates \( \Gamma_k \), so the characteristic frequencies become
\[ \bar{\omega}_+ \approx \frac{1}{\tau_0} (1 + 2\xi^2_{ve} k^2), \tag{79} \]
\[ \bar{\omega}_- \approx \Sigma^G_k(0). \tag{80} \]

The resultant structure factor is approximated as
\[ G^{\psi\psi}_k(t) \approx \exp[-\Sigma^G_k(0)t]. \tag{81} \]

That is, the critical mode associated with the concentration fluctuations can be free from the coupling with the viscoelasticity very near the critical point. Then, using eqs.(51), (70) and (74), the long-wavelength expression of the diffusion constant is given by
\[ D = \frac{k_B T}{6\pi \xi (\eta_p + \eta_0)} \left( 1 + \frac{\eta_p}{\eta_0 A} \right). \]
We point out that the temperature regime where the hydrodynamic interaction dominates the diffusion process \( (\Sigma^G_{\mathbf{k}}(0) \gg \Gamma_{\mathbf{k}}) \) becomes narrower as the molecular weight increases, since \( \eta_p \propto M_w^{3.31} \).

4.3 Renormalized Viscosity

In the previous sub-section, we assumed that the shear viscosity does not show the critical anomaly. However, as is well known, the shear viscosity exhibits a weak divergence at the critical point. In this sub-section, we investigate the critical anomaly of the shear viscosity. We can evaluate the self energy \( \Sigma^H_{\mathbf{k}}(0) \) by putting \( \omega = 0 \) in (67):

\[
\Sigma^H_{\mathbf{k}}(0) = \frac{k_B T}{4 \rho} \int_0^\infty ds \int dp \, p^2 [1 - (\hat{\mathbf{p}} \cdot \hat{\mathbf{k}})^2] \times \frac{1}{|\psi_{\mathbf{k}-\mathbf{p}|^2}} \frac{1}{|\psi_{\mathbf{p}|^2}} \langle \hat{\mathbf{p}} \rangle G_{\mathbf{p}}^{\psi \psi}(s) G_{\mathbf{k}-\mathbf{p}}^{\psi \psi}(s).
\]

(83)

Retaining the lowest power of \( k \), the resultant integration can be performed analytically, using the results obtained in the previous sub-section:

\[
\rho k^2 \Sigma^H_{\mathbf{k}}(0) \approx \frac{k_B T \xi^4}{30 \pi^2} \int_0^{\Lambda_0} dp \, \frac{p^6}{1 + \xi^2 p^2} \frac{1}{\Sigma^G_{\mathbf{p}}(0)},
\]

(84)

where \( \Lambda_0 \) is the microscopic cut-off wave number. The above integrand can be estimated as

\[
\frac{k_B T \xi^4}{30 \pi^2} \frac{p^6}{1 + \xi^2 p^2} \frac{1}{\Sigma^G_{\mathbf{p}}(0)} \approx \frac{\eta_0 + \eta_p}{5 \pi (1 + \frac{2 \eta_p}{\eta_0 A})} \xi^5 p^4, \quad (p \ll \frac{1}{\xi}),
\]

(85)

\[
\approx \frac{8(\eta_0 + \eta_p)}{15 \pi^2} \frac{1}{p + \tau_p^2}, \quad \left( \frac{1}{\xi} \ll p \ll \frac{1}{\xi_b} \right),
\]

(86)

\[
\approx \frac{8 \eta_0}{15 \pi^2} \frac{1}{p}, \quad (p \gg \frac{1}{\xi_b}),
\]

(87)

where \( \tau = 8 \eta_p \xi / 3 \pi \eta_0 A \). In the case \( \eta_p \gg \eta_0 \) eqs.(51) and (70) give

\[
\tau \approx \left( \frac{\eta_p}{\eta_0} \right)^\frac{1}{2} \xi_{ve} \approx \left( \frac{\eta_p}{\eta_0} \right) \xi_b.
\]

(88)

The anomalous part of the shear viscosity \( \Delta \eta \) is given by

\[
\Delta \eta = \frac{\rho}{k^2} \Sigma^H_{\mathbf{k}}(0).
\]

(89)

Thus, we obtain the total shear viscosity in the following form,

\[
\eta = \bar{\eta} + \Delta \eta \approx \bar{\eta} \left\{ 1 + \frac{8}{15 \pi^2} \left[ \frac{3 \pi}{40} \frac{1}{1 + \frac{2 \eta_p}{\eta_0 A}} + \ln \left( \frac{\xi + \tau}{\xi_b + \tau} \right) + \frac{\eta_0}{\bar{\eta}} \ln (\xi_b \Lambda_0) \right] \right\},
\]

(90)
where $\bar{\eta} = \eta_0 + \eta_p$ is the bare shear viscosity. In Fig.2 we plot the reduced shear viscosity $\Delta \eta / \bar{\eta} = \eta / \bar{\eta} - 1$ as a function of $\eta_p / \eta_0$. It is evident that the critical divergence of the shear viscosity is suppressed as the molecular weight increases.

For $\eta_p \gg \eta_0$ and $\xi_{ve} \approx \xi$, it is readily shown that the resultant renormalized shear viscosity does not exhibit critical anomaly.

$$\frac{\eta}{\bar{\eta}} \approx 1.$$ (91)

For $\eta_p \approx \eta_0$ and $\xi \gg \xi_{ve}$, where the viscoelasticity is relatively weak, we obtain the anomalous shear viscosity as follows:

$$\frac{\eta}{\bar{\eta}} \approx 1 + \frac{8}{15\pi^2} \ln \left( \frac{\xi_0}{(\xi_b \Lambda_0)^{\frac{4}{3}}} \right).$$ (92)

Because of the small coefficient of the logarithmic term, it may well be exponentiated with the small exponent $x_\eta = 8/15\pi^2 \approx 0.054$ as

$$\frac{\eta}{\bar{\eta}} \approx \left( \frac{\xi_0}{(\xi_b \Lambda_0)^{\frac{4}{3}}} \right)^{x_\eta}.$$ (93)

In the low molecular weight limit ($\eta_p = 0$) the expressions reduce to those of the simple classical fluids, with $y_c = x_\eta \nu \approx 0.034$.

The above results are due to the existence of an extra length-scale $\xi_{ve}$ intrinsic to the viscoelasticity. As is well known, in the case of classical fluids the behavior of the critical anomaly of the shear viscosity does not depend on the detail of the material. That is, the behavior of the critical anomaly does not depend on the material parameter, and is universal (model H). Contrary to this, as shown in the present analysis, in the case of polymer solutions the critical divergence of the shear viscosity strongly depend on the molecular weight $M_w$. Now, a few comments must be made on those points. When the correlation length $\xi$ is very large compared with the other length scale, it is shown that our results certainly exhibit the universal behavior. However, as noted by Tanaka, it is difficult to experimentally access such a temperature region for polymer solutions whose polymer has a very high molecular weight. In this sense we can say that the model H universality does not hold, at least in a practical sense.

§5. Conclusions and Remarks

In this article we have investigated the dynamic critical phenomena of polymer solutions. Based on the mode coupling theory, we derived a set of self-consistent equations for the self energies, taking the non-linear hydrodynamic interaction into account. Renormalizing the non-linear hydrodynamic interaction terms which are important in the vicinity of the critical point, the transport coefficients were calculated.
Our analysis predicts that the critical divergence of the shear viscosity is suppressed as the molecular weight increases. This effect was indeed observed experimentally by Tanaka, et al.\textsuperscript{15)} At the present stage the quantitative comparison with the experiments is difficult in the following reasons. There are many unknown parameters (for instance, $\eta_p$ and $\xi_b$ etc.) which cannot be evaluated explicitly. In addition, in their paper\textsuperscript{15)} they introduced an effective exponent $y_c$ and then discussed the singularity of the shear viscosity. However, this does not relate directly to our result, eq. (90).

We have also calculated the diffusion constant eq.(82) and the dynamic structure factor $G_{\psi\psi}^\psi(t)$ with the renormalized relaxation rates $\tilde{\omega}_\pm$, eq.(78), by the non-linear hydrodynamic interaction. Those are new results for critical polymer solutions. I expect that the present theoretical analysis would stimulate further experimental studies.

In the present analysis we have used the Markov approximation in order to evaluate the self-energies. Previously several authors investigated the memory effects in the critical dynamics of classical fluids and predicted that the effect has small contributions to the kinetic coefficients.\textsuperscript{33, 34)} These theoretical predictions have been successfully confirmed by the experiments.\textsuperscript{35)} In the case of polymer solutions the separation of the time scale between concentration fluctuations and the velocity is not clear as in the case of classical fluids. Hence there is a possibility that the viscoelasticity amplifies the frequency dependence of the kinetic coefficients. We will present more detailed studies for this elsewhere.\textsuperscript{36)}

Finally, we note the following. It is well known that the dynamical asymmetry coupling ($\alpha \neq 0$) between the concentration fluctuations and the viscoelastic stress gives the so-called stress-diffusion coupling.\textsuperscript{17, 19)} In addition to this effect, by the present linear response analysis (§3), it has become apparent that the hydrodynamic relaxation process is also drastically influenced by the dynamical asymmetry coupling between the velocity field and the viscoelastic stress. The calculated bare shear viscosity has a wave number dependence as seen from eq.(48).

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32) In the same way, in the study of the dynamic critical phenomena of classical fluids, exponentiating eq.(1) can give the dynamic exponent of the shear viscosity,6) which was first introduced in the study by the dynamic renormalization group theory.4) Because the second term is smaller than the first in Eq.(1), such a procedure is allowed under actual experimental conditions (ξ ≲ 10^{-3} cm). However, there has been no definite conclusion which of the logarithmic divergence or the exponential divergence is correct. By the way, in the present study, we estimate the viscosity anomaly as eq.(90). Due to the viscoelasticity, the expression is more complex than that in the case of classical fluids, and the magnitude of each term strongly depends on parameters, such as A and ηp/ηo. Therefore, it is generally difficult to obtain the multiplicative form by exponentiating eq.(90). Moreover, the meaning of the multiplicative anomaly of the shear viscosity is still unclear in the study of critical polymer solutions. Hence, we leave eq.(90) as it is.
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Figure Captions

Fig.1. Reduced self energy \( Q(x, A, \eta_p/\eta_0) = [K(x) + \frac{2\eta_p}{\eta_0} F(x, A)]/x^2 \) from eq.(68) (solid line). The asymptotic form (broken line) is also plotted. We note that the dynamic scaling is broken down and the self energy cannot be expressed by the Kawasaki scaling function (dotted line), that is definite in (a) and (d) where the viscoelasticity is relatively strong.

Fig.2. Reduced shear viscosity \( \Delta \eta/\bar{\eta} = \eta/\bar{\eta} - 1 \) vs \( \eta_p/\eta_0 \) for various values of \( A \). Here we set \( \Lambda_0 \xi_b = 10 \) and use eq.(70). It is evident that the divergence of the shear viscosity is suppressed as the molecular weight is increased.
