

Probing structural relaxation in complex fluids by critical fluctuations

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Complex fluids, such as polymer solutions and blends, colloids and gels, are of growing interest in fundamental and applied soft-condensed-matter science. A common feature of all such systems is the presence of a mesoscopic structural length scale intermediate between atomic and macroscopic scales. This mesoscopic structure of complex fluids is often fragile and sensitive to external perturbations. Complex fluids are frequently viscoelastic (showing a combination of viscous and elastic behaviour) with their dynamic response depending on the time and length scales. Recently, non-invasive methods to infer the rheological response of complex fluids have gained popularity through the technique of microrheology, where the diffusion of probe spheres in a viscoelastic fluid is monitored with the aid of light scattering or microscopy. Here we propose an alternative to traditional microrheology that does not require doping of probe particles in the fluid (which can sometimes drastically alter the molecular environment). Instead, our proposed method makes use of the phenomenon of "avoided crossing" between modes associated with the structural relaxation and critical fluctuations that are spontaneously generated in the system.

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A liquid mixture in the vicinity of a critical point of mixing exhibits large concentration fluctuations. The dynamics of such critical concentration fluctuations in molecular liquids is well understood: the fluctuations decay exponentially with a diffusive relaxation time [1]

$$\tau_q = \frac{1}{D(q, \xi)q^2}, \quad (1)$$

where q is the wave number of the critical fluctuations, ξ is the spatial correlation length of the fluctuations and D is the mesoscopic (q -dependent) diffusion coefficient. D vanishes at the critical point in the limit of zero wave number approximately as $\xi^{-1} \sim \varepsilon^{0.63}$, where $\varepsilon = (T - T_c)/T$, the reduced distance between the temperature T and the critical temperature T_c . In molecular fluids, the q -dependent diffusion coefficient is well described by the mode-coupling theory of critical dynamics [2, 3].

$$D(q, \xi) = \frac{k_B T}{6\pi\xi\eta_{\text{app}}} \frac{K(q, \xi)}{q^2} \left[1 + \left(\frac{q\xi}{2} \right)^2 \right]^{\frac{z_\eta}{2}} \Omega\left(\frac{\xi}{\xi_D}\right), \quad (2)$$

where k_B is Boltzmann's constant and where the apparent viscosity η_{app} is expected to be equal to the solution

viscosity η measured by macrorheology; $z_\eta \simeq 0.065$ [4] is a universal dynamic scaling exponent. The function $K(q, \xi)$ is a universal (Kawasaki) function with $K(q\xi \rightarrow 0) = 1$; the function $\Omega(\xi/\xi_D) = 2/\pi \arctan(\xi/\xi_D)$ is an approximated dynamic crossover function, where ξ_D is a cutoff length for the critical fluctuations [5, 6],

However, new phenomena emerge in a complex fluid where ξ_D is a mesoscopic length that may compete with the correlation length ξ of the concentration fluctuations. The presence of two mesoscale lengths in near-critical complex fluids causes the appearance of two dynamic modes: one will be a diffusive decay of the critical concentration fluctuations and another one will be a structural relaxation mode, which often reveals itself as viscoelastic relaxation. The decay time of the diffusive mode can be tuned over a broad range of time scales by varying the reduced temperature ε , so that it may intersect the structural relaxation time, which is insensitive to the proximity to the critical point. As a consequence it becomes possible to probe structural relaxation in complex fluids by dynamic light scattering of critical fluctuations. This method is an alternative to the traditional microrheology [7–9] that requires doping of probe particles in the fluid.

As an illustration of this principle, we have performed accurate light-scattering measurements of solutions of nearly monodisperse polystyrene (with molecu-

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lar weights M ranging from 10^4 to 10^7) in cyclohexane [10, 11]. The major result of our study is that the critical dynamics in polymer solutions appears to be very different from that in molecular fluids. Even for a modest polystyrene molecular weight of 195,900, with the dynamic correlation function obeying a single-exponential decay, the apparent viscosity η_{app} extracted from dynamic light scattering (DLS) (on the basis of Eq. (2) with the correlation length ξ determined by static light scattering [10]) is vastly different from both the macroscopic viscosity of the solution and the viscosity of the solvent (Fig.1). But in terms of this apparent ("mesoscopic")

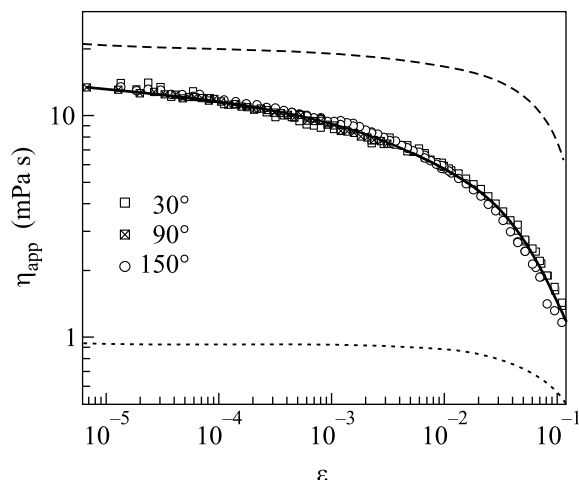


Fig.1. Apparent mesoscopic viscosity of a solution of polystyrene ($M = 195,900$) in cyclohexane as a function of $\varepsilon = (T - T_c)/T$ obtained by fitting the experimental light-scattering data to the mode-coupling theory. The dotted curve represents the viscosity of the solvent (cyclohexane) and the dashed curve represents the macroscopic viscosity of the same solution [12]

viscosity, the mesoscopic diffusion coefficient at various angles can be well described by Eq. (2) (lines through the symbols, Fig.2). The pertinent question is: what is the physical meaning of this "mesoscopic" viscosity determined with DLS? Disagreements between the predictions of the mode-coupling theory for molecular fluids and the DLS data in near-critical polymer solutions have also been noted by others [12, 13], but have not yet been explained.

We have observed an even more dramatic change in dynamics in high molecular-weight ($M = 10^6$ and higher) polymer solutions, where the dynamic correlation function turns out to deviate from a single-exponential decay and where two dynamic modes are clearly present. Far from the critical point, a fast mode dominates, while close to the critical point a slow mode dominates. Between these extremes, the data can be

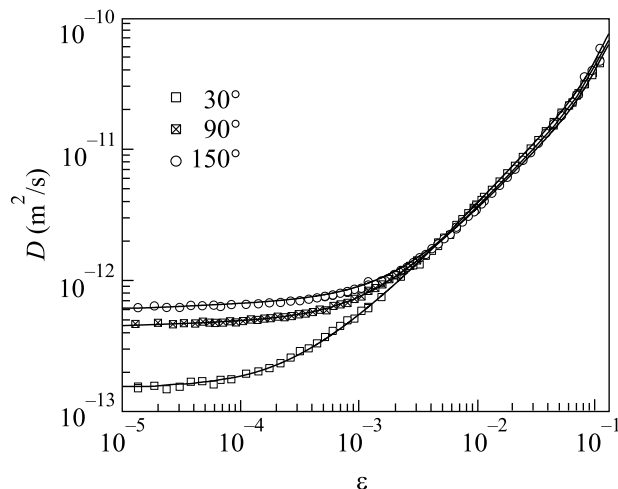


Fig.2. Mesoscopic diffusion coefficient of a solution of polystyrene ($M = 195,900$) in cyclohexane as a function of $\varepsilon = (T - T_c)/T$ measured at three scattering angles. The symbols represent experimental data, while the curves represent the critical contribution predicted by mode-coupling theory with the mesoscopic viscosity shown in Fig.1

approximated by a sum of two exponentials, indicating contributions from both modes. The presence of two dynamic modes near the critical temperature appears to be a universal feature in macromolecular systems and has been observed also by Ritzl et al. [14] for an $M = 1$ million polystyrene solution in cyclohexane and more recently by Tanaka et al. [15] for an $M = 4$ million polystyrene solution in diethyl malonate. These modes are effective dynamic modes, neither of which is purely viscoelastic (dictated by polymer chain dynamics) or purely diffusive (associated with the decay of critical fluctuations). Instead, the two observed modes emerge from a coupling of diffusive and viscoelastic modes, which belong to two different dynamic universality classes, pertaining to conserved and non-conserved order parameters [16]. The challenge is to quantitatively understand this coupled dynamic crossover behaviour. A starting point in explaining the dynamics is the Brochard-De Gennes theory [17–19], which predicts a coupling of diffusion and chain relaxation in polymer solutions that has been subsequently detected experimentally in non-critical polymer solutions [20–22].

We submit that the Brochard-De Gennes theory can be applied to any system with dynamic coupling between conserved and non-conserved order parameters. Phenomenologically, it follows from this theory that the time-dependent intensity correlation function is the sum of two exponentials:

$$g_2(t) = 1 + \left\{ f_+ \exp\left[-\frac{t}{\tau_+}\right] + f_- \exp\left[-\frac{t}{\tau_-}\right] \right\}^2, \quad (3)$$

with two decay times (slow τ_- and fast τ_+) and with corresponding amplitudes (f_{\pm}) given by:

$$\frac{1}{\tau_{\pm}} = \frac{1 + q^2 \xi_{ve}^2 + \frac{\tau_{ve}}{\tau_q} \pm \sqrt{\left(1 + q^2 \xi_{ve}^2 + \frac{\tau_{ve}}{\tau_q}\right)^2 - 4 \frac{\tau_{ve}}{\tau_q}}}{2\tau_{ve}}, \quad (4)$$

$$f_{\pm} = \frac{\frac{\tau_{ve}}{\tau_{\pm}} - \left(1 + q^2 \xi_{ve}^2\right)}{\frac{\tau_{ve}}{\tau_+} - \frac{\tau_{ve}}{\tau_-}}. \quad (5)$$

In Eq. (4) τ_{ve} is the q -independent viscoelastic relaxation time, τ_q is the q -dependent diffusion relaxation time, and ξ_{ve} the mesoscopic viscoelastic length [23]. The above theory indeed grasps the essential features of our data (Figs. 3 and 4), if we use ξ_{ve} and τ_{ve} as ad-

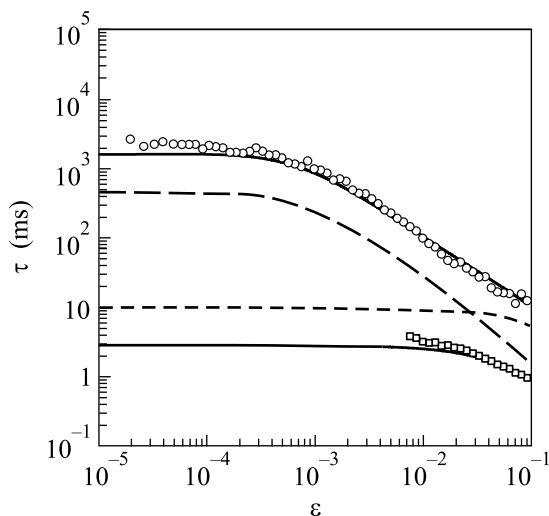


Fig.3. Dynamic modes in a solution of polystyrene ($M = 11.4$ million) in cyclohexane for q , corresponding to a scattering angle of 30° . Open symbols represent the experimental relaxation times of the two observed modes. The solid curves represent the relaxation times of the effective “slow” and “fast” modes, calculated with Eq. (4). The long-dashed curve represents the uncoupled critical-diffusion decay time. The short-dashed curve represents the uncoupled viscoelastic relaxation time

justable parameters. In addition, to obtain $\tau_q = 1/Dq^2$, we need to use the apparent mesoscopic viscosity η_{app} in Eq. (2). The predictions for the two uncoupled modes (pure diffusion and pure viscoelastic relaxation) are indicated by the dashed curves in Fig.3. While the diffusion

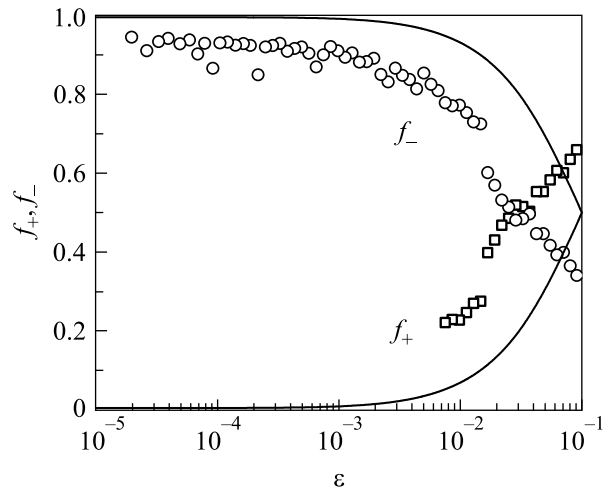


Fig.4. Amplitudes of the two effective dynamic modes as a function of $\varepsilon = (T - T_c)/T$ in a near-critical polymer solution. Solid curves are theoretical predictions for the amplitudes (Eq. (5))

relaxation time changes rapidly when the critical point is approached, the viscoelastic relaxation time exhibits a regular dependence on temperature. While the original uncoupled modes would cross each other at a certain temperature, the coupling produces two effective modes that “avoid crossing” each other very much similar to the well known avoided crossing of two coupled energies [24]. Therefore, the microrheological characteristics can be deduced from scattering data in a near-critical fluid, since one can vary the diffusion relaxation time over many orders, thus probing the relevant viscoelastic times over the same range.

While ξ_{ve} (as expected [23, 25]) appears to be proportional to the viscosity, it was not clear a priori which viscosity is the appropriate quantity, the mesoscopic η_{app} or the macroscopic η at zero shear rate. Our study has shown that ξ_{ve} is proportional to the apparent (“mesoscopic”) viscosity measured by DLS. A further notable point is the shift in Fig.3 between the calculated diffusion mode (long-dashed curve) and the observed slow mode (τ_- , solid curve). The data suggest that τ_- is slowed down at nanoscales by a factor $q^2 \xi_{ve}^2$ with respect to the diffusion mode. For example, at $M = 11.4$ million and a scattering angle of 30° , where length scales of about $q^{-1} = 137$ nm are probed and where ξ_{ve} reaches 200 nm, the slow mode is shifted from 0.4 s to 1.5 s. We may attribute this anomalous slowing down of the fluctuations to “diffusion trapped by viscoelasticity at the nanoscale” and we expect this effect to be ubiquitous in viscoelastic systems. Note that this effect of additional slowing down at smaller scales (large q) is opposite to the famous critical slowing down, which becomes more

pronounced at larger scales (small q). In Fig.4 the experimental amplitudes of these effective dynamic modes are compared with the theoretical ones calculated with Eq. (5). We submit that our interpretation of the coupled modes on the basis of the Brochard-De Gennes theory does account for the essential physics of the phenomenon. The analysis of the observed avoided-crossing of two coupled modes has a good sensitivity because the amplitudes of the two effective modes become of the same order of magnitude in the avoided-crossing domain (Fig.4).

The key results obtained in our study are significant far beyond just the near-critical polymer solutions investigated. The coupling between diffusion-like and structure relaxation modes is expected whenever such modes are close to each other and thus scanning the diffusivity decay times by any means (varying composition, temperature, or pressure) will reveal the structural relaxation. Our results are relevant for a variety of complex fluids in which critical phenomena couple with a mesoscopic structure and/or with viscoelastic relaxation. These include polymers in supercritical fluids [26], polymer blends [27], polymer solutions under shear [28], and microemulsions [29, 30], as well as systems important in the life sciences, such as solutions of polyelectrolytes or biopolymers [31, 32].

We conclude by highlighting the possible practical applications of studying the coupling between diffusive relaxation of critical fluctuations and structural relaxation. Because of this coupling, dynamic light scattering of critical fluctuations becomes a new tool for measuring the rheological properties of near-critical complex fluids. That is, by performing non-invasive DLS measurements on a sample, we can obtain quantitative information concerning its microrheological properties. Our proposed approach may be termed “critical microrheology” and does not require the addition of probe particles to the fluid. The uniqueness of critical microrheology is its ability to scan diffusive decay time of fluctuations at a given length scale q^{-1} over several orders of magnitude, and thereby probe viscoelastic relaxation as an intrinsic fluid property. Moreover, instances have been reported where microrheological measurements are inconsistent with macroscopic rheology [33]. “Critical microrheology” experiments may clarify the nature and extent of these discrepancies. By selecting appropriate solvents for bringing systems into a near-critical state one should be able to probe structural relaxation of a variety of macromolecular species in solutions.

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