the sound velocity in the normal state and in the superconducting state. Such an experiment could reveal the effect of the conduction electrons on the transverse relaxation time.

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Dynamics of Collective Fluctuations and Brownian Motion in Polymer Melts

D. Richter, A. Baumgärtner, and K. Binder
Institut für Festkörperforschung, Kernforschungsanlage Jülich, D-5170 Jülich, Federal Republic of Germany

and

B. Ewen
Institut für Physikalische Chemie, Universität Mainz, D-6500 Mainz, Federal Republic of Germany

and

J. B. Hayter
Institut Laue-Langevin, F-38042 Grenoble, France

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The dynamic structure factor of entangled polymer chains in a melt is investigated by neutron spin-echo techniques and by computer simulations of related models. Over a wide range of wave vectors q the structure factor decays with time t exponentially with a rate $\propto q^2 t^{1/2}$, in agreement with the simple Rouse model. Reptation is found to be effective only for simulations of chains in a frozen-in environment, under otherwise identical conditions.

PACS numbers: 61.40.Km, 61.12.-q, 64.60.Ht, 66.10.Cb

The diffusive motions of polymers in a melt are commonly modelled as reptation processes:[1-4] There the flexible polymer chain is thought to move like a snake in a "tube" formed by topological constraints, so-called "entanglement points," imposed by the other chains. This mechanism contrasts to the much simpler Rouse model,[5] describing the Brownian motion of an unconstrained chain in a heat bath. However, because of the complexity of dense polymer systems, it is not clear whether one of these highly simplified phenomenological models is adequate. In this Letter the dynamic structure factor of polymer melts is obtained from both experiment and computer simulations. A comparison with predictions of these two models will clarify which model is appropriate.

In the Rouse model the mean-square displacement $\langle r^2(t)\rangle$ of any monomer along the chain increases with time t as $\langle r^2(t)\rangle \propto l^2\sqrt{Wt}$, where l is a microscopic length of the order of monomer linear dimensions, and W an associate rate. This $t^{1/2}$ law shows up both in the incoherent and coherent structure factor[6]:

$$S_{\text{inc}}(\vec{q}, t) = \exp[-\tfrac{1}{6}q^2\langle r^2(t)\rangle], \tag{1}$$

$$S_{\text{coh}}(\vec{q}, t) = \frac{1}{N}\sum_{i=1}^{N}\sum_{j=1}^{N}\exp\{-\tfrac{1}{6}q^2\langle[\vec{r}_i(0)-\vec{r}_j(t)]^2\rangle\}, \tag{2}$$

$$\langle[\vec{r}_i(0)-\vec{r}_j(t)]^2\rangle \cong |i-j|\,l^2 + 2l^2(\sqrt{Wt}/\pi)\,g((j-i)^2/4Wt),\quad g(u) = \int_1^\infty dx\,x^{-2}e^{-ux^2}, \tag{3}$$

where the indices i and j label the N monomers along the chain. Thus $S_{\text{coh}}(\vec{q}, t)$ describes collective chain relaxations. Equations (1)–(3) are valid for wave vector q much larger than the inverse radius of gyration R of the coil. There the internal dynamics of the chain rather than its diffusion as a whole is probed.[7] In this regime both $S_{\text{coh}}(q, t)$ and $S_{\text{inc}}(q, t)$ *decay exponentially* with a rate proportional to $(ql)^2(Wt)^{1/2}$ for long times.

For the reptation model of a chain with a density ρ_e of entanglement points along the chain Rouse relaxation is predicted only for q larger than the inverse tube diameter, where displacements not yet restricted by entanglements are probed. For smaller q, $S_{\text{inc}}(q, t)$ relaxes with a $t^{1/4}$ law[1],

$$\langle r^2(t)\rangle \propto l^2\rho_e^{1/2}(Wt)^{1/4}. \tag{4}$$

Considering "local reptation processes" of the chain in its tube, de Gennes[4] suggested a different behavior for the collective relaxation of one chain in the network of the other chains: The coherent scattering function exhibits a strongly *non-exponential decay*. With use of $S_{\text{coh}}(q, 0) \sim (ql)^{-2}$, his results retain simple expressions for two limiting cases:

$$-\ln\frac{S_{\text{coh}}(q, t)}{S_{\text{coh}}(q, 0)} \propto \begin{cases} (ql)^4(Wt)^{1/2}, & (ql)^2(Wt)^{1/2} \ll 1 \qquad \text{(5a)} \\ (Wt)^{-1/2}, & (ql)^2(Wt)^{1/2} \gg 1, \quad t \ll \tau_{\text{rep}}. \qquad \text{(5b)} \end{cases}$$

During the time $\tau_{\text{rep}} \propto N^2/\rho_e W$ the chain creeps out of its original tube, and hence the chain diffusivity is $D \propto \tau_{\text{rep}}^{-1} \propto N^{-2}$. While experimental evidence exists[3] for the resulting dependence $D \propto M_w^{-2}$ on molecular weight, the predictions of Eq. (5) relating to the internal dynamics of the chain have not yet been checked experimentally.

We have measured the quasielastic neutron small-angle scattering from deuterated polymer melts containing 5% protonated fractions in the q range of interest, $0.64 \leqslant qR \leqslant 8.6$, with use of the neutron spin echo spectrometer IN11 at the Institute Laue-Langevin in Grenoble. For a narrow enough incident wavelength distribution this novel technique directly yields[8] $S_{\text{coh}}(\vec{q}, t)$, the time being proportional to the applied guide field H (100 Oe $\simeq 1.9\times10^{-9}$ sec). At a neutron wavelength of 8 Å the practical q range was $0.026 < q < 0.132$ Å^{-1}, the time range being 10^{-9} sec $< t < 10^{-8}$ sec. Three different melts were studied at 100 C all containing deuterated polydimethylsiloxane (PDMS) with $M_w = 60\,000$ as a host, and protonated chains with different molecular weight, $M_w = 60\,000$, $30\,000$, and 3800. Compared to the strong small-angle scattering the background from the deuterated matrix as well as the incoherent scattering from the protonated polymers was found to be negligibly small.

The normalized resolution corrected[9] polarization decay $P(H) = S_{\text{coh}}(\vec{q}, t)/S_{\text{coh}}(\vec{q}, 0)$ is shown in Fig. 1. For q between 0.03 and 0.1 Å^{-1} we find a linear variation of $\ln[-\ln P(H)]$ with $\ln H$, the slope being close to $\frac{1}{2}$. Thus $S(\vec{q}, t)$ is consistent with an *exponential* form with a decay rate $\alpha(q)$, $S_{\text{coh}}(\vec{q}, t)/S_{\text{coh}}(\vec{q}, 0) = \exp[-\alpha(q)t^{1/2}]$. Using Eq. (3) and $l^2 = 10$ Å^2, we estimate $W \approx 3\times10^{11}$ sec^{-1}. At the largest q, $q = 0.13$ Å^{-1}, the data perhaps indicate a crossover to a larger exponent. This effect may be due to a crossover to hydrodynamic interactions, which would yield an exponent $\frac{2}{3}$ rather than $\frac{1}{2}$ (Refs. 8 and 10) but are expected to be screened over atomic distances in the melt. The rate $\alpha(q)$ is roughly consistent with a law $\alpha(q) \propto q^2$ (Fig. 2) with exponents varying between 1.7 and 2.1. With decreasing molecular weight

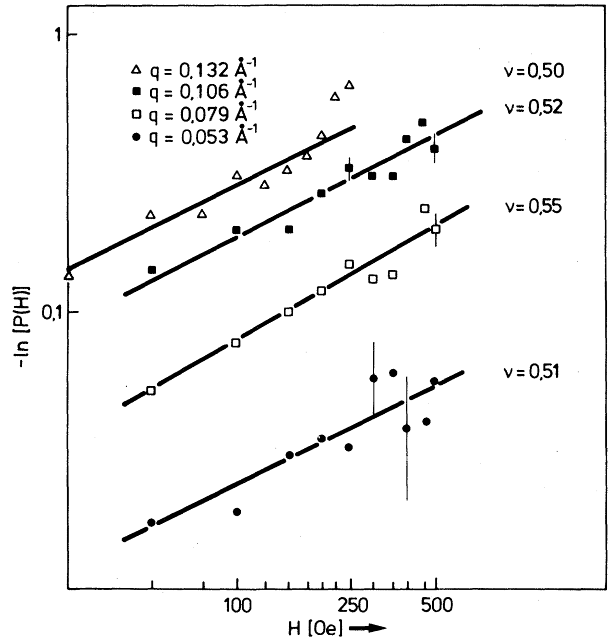

FIG. 1. Polarization decay $P(H) = S_{\text{coh}}(\vec{q}, t)/S_{\text{coh}}(\vec{q}, 0)$ obtained from 5% protonated PDMS ($M_w = 60\,000$) in deuterated PDMS ($M_w = 60\,000$) for different q plotted in a double-logarithmic scale. ν gives the slope of ln $[-\ln P(H)]$ vs $\ln H$.

the relaxation rate slightly increases, and at the same time its q dependence flattens. There should be *no q dependence* if the *nonexponential* law, Eq. (5b), were valid!

Thus, although the q range probed was sufficient to cover nearly the entire range of internal modes of the chains, with the exception of monomer relaxation, there is no evidence for the reptation mechanism. Rather the relaxation of *all* internal modes seems to be consistent with the Rouse model, indicating that reptation is not yet effective for the time scales studied.

In order to elucidate this situation further, we have performed a Monte Carlo simulation of a polymer melt. Of course, this can be done for very simplified models only. We have chosen a model[11] of chains consisting of $N-1$ rigid links of length l freely joined together at the N beads at arbitrary angles. Thus each link may represent, say, ten successive monomers of a physical chain. We put $n=10$ chains in a cubic box of linear dimensions $L = l\sqrt{N}$ with periodic boundary conditions. As an interaction between beads a distance r_{ij} apart we arbitrarily assume a Lennard-Jones potential, $U_{ij} = 4\epsilon[(\sigma/r_{ij})^{12} - (\sigma/r_{ij})^6]$, with $\sigma = 0.4l$. ϵ sets the temperature scale, and we typically choose $k_BT/\epsilon = 3$ since then single chains

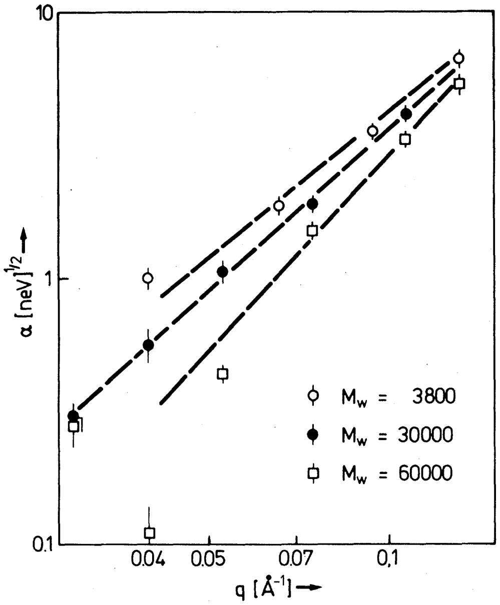

FIG. 2. Relaxation rate $\alpha(q)$ from a fit of the spectra with $\exp[-\alpha(q)t^{1/2}]$ for three different molecular weights of protonated PDMS in a deuterated host ($M_w = 60\,000$).

are still well above their collapse transition temperature.[11]

Dynamics is associated to the model by randomly selecting a bead and attempting a rotation of its adjoining links by a randomly chosen angle. In the transition probability, we not only include the above potential via the appropriate Boltzmann factor,[11] but also forbid all rotations during which any links would intersect, thus simulating entanglement restrictions. The latter are quite effective in our case: The relaxation becomes slower by about an order of magnitude than otherwise. Studying time scales up to 10^5 Monte Carlo steps (MCS) per bead, we had to use N as small as $N=17$. However, such small N for this model already suffice to see the large N asymptotic behavior, e.g., laws $R \propto N^{0.59}$ for single "swollen" chains, etc.[11]

Again the relaxation is well accounted for by the Rouse model (Fig. 3): $\langle r^2(t)\rangle \propto t^{1/2}$ holds over more than two decades of time, and Eq. (3) fits the data well and reveals a characteristic rate $W \sim 40$ MCS. With the experimental W we have 1 MCS $\sim 10^{-13}$ sec in the real melt. Of course, the relaxation $\propto Dq^2t$ due to the diffusion of the chain as a whole seen in the simulation at late stages is not included in Eq. (3). No evidence of reptation is seen, in agreement with experiment. This is true also for much lower temperatures and

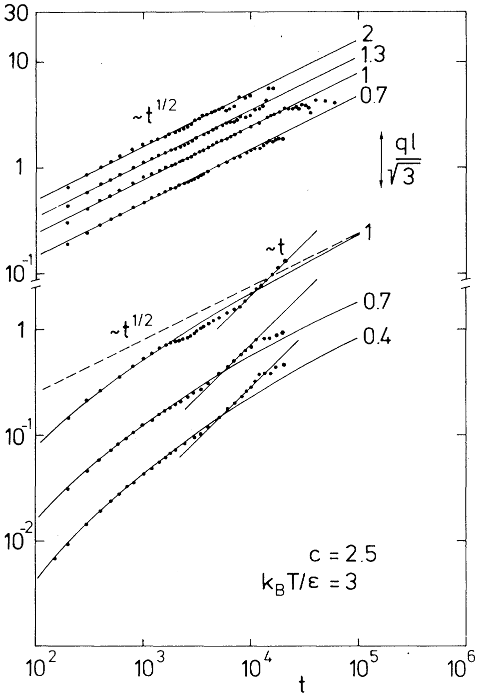

FIG. 3. Log-log plot of Monte Carlo results for $S_{\rm inc}(\vec{q},t)$ (upper part) and $S_{\rm coh}(\vec{q},t)/S_{\rm coh}(\vec{q},0)$ (lower part) vs time for $k_BT/\epsilon = 3$, a "concentration" $c = Nn/(L/l)^3 = 2.5$, and various q. Solid curves represent the Rouse model [Eq. (2)], where the rate W was adjusted (W being $0.02-0.03$, for our time units).

much higher densities, where instead a transition to a glasslike state occurs, where all displacements are negligibly small for the accessible times.[12]

Of course, for very short chains the reptation mechanism breaks down because then the number of entanglement points per chain $N\rho_e$ becomes of order unity.[1,3] In order to show that our failure to see reptation is not just due to this trivial reason we have done a simulation, again for the first time, where a chain moves in an environment of fixed obstacles. This is the situation for which Eqs. (4) and (5) have been derived.[1,4] To this end, we use an equilibrated configuration of the melt and freeze in the configuration of all chains apart from one mobile chain. Figure 4 shows that now the reptation model is indeed adequate: A rate $\propto q^2t^{1/4}$ is seen for $S_{\rm inc}(q,t)$, as expected from Eqs. (1) and (4). The somewhat quicker initial rate may be a remnant of Rouse relaxation over very small scales. For $(ql)^2\sqrt{Wt} \ll 1$ the behavior of $S_{\rm coh}(q,t)$ is consistent with Eq. (5a). But for larger q's and longer times in contrast to Eq. (5b) a crossover again to a rate proportional to $q^2t^{1/4}$ is observed. This result reflects the fact that for long times $\langle |r_i(0)-r_j(t)|^2\rangle$ [cf. Eq. (3)] must evolve with the same asymptotic time dependence as $\langle r^2(t)\rangle \propto t^{1/4}$ and hence $S_{\rm coh}(q,t)$ should decay as $S_{\rm inc}(q,t)$ asymptotically.

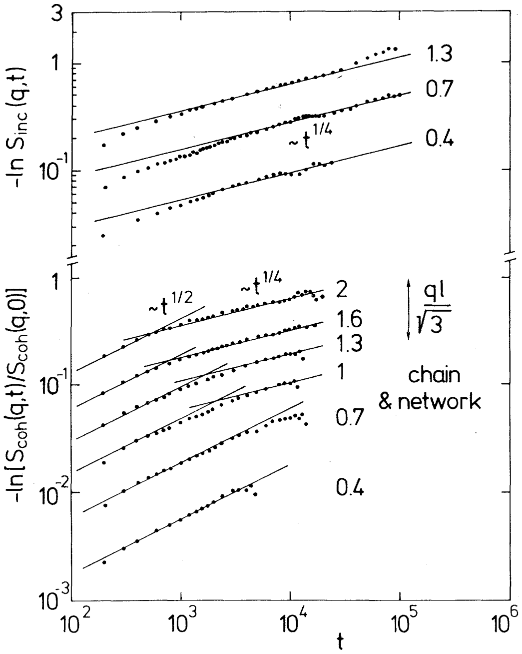

FIG. 4. Log-log plot of Monte Carlo results for $S_{\rm inc}(\vec{q},t)$ (upper part) and $S_{\rm coh}(\vec{q},t)/S_{\rm coh}(\vec{q},0)$ (lower part) vs time for a chain in a frozen-in network of other chains at $k_BT/\epsilon = 3$ and $c = 2.5$, for several values of q.

In conclusion, internal modes of polymers in melts cannot be explained by reptation, but are in qualitative accord with the Rouse model—which, however, can neither explain diffusion[3] nor viscosity[2] of melts. Thus a new approach to the dynamics of entangled polymers is called for. We suggest that the coupling between the fluctuations of a chain to the fluctuations of the surrounding chains forming its tube needs to be considered. In fact, even if the topology of entangled chains is not changed, the network of entangled chains may be deformed because the actual positions of entanglement points need not be fixed when all chains move simultaneously.

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Correlation between Adatom-Adatom Pair Interaction and Adlayer Superstructure Formation: Si on W{110}

T. T. Tsong and Rodrigo Casanova
Physics Department, The Pennsylvania State University, University Park, Pennsylvania 16802

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Pair energies for Si adatoms on the W{110} for several bond lengths were obtained by direct field-ion–microscopy observations. Maximum binding occurred at a distance $\sqrt{2}a$ in the $[1\bar{1}0]$ and maximum antibinding at a in the $[001]$; a is the lattice constant. From the data, the two-dimensional binding energy per adatom in an adlayer can be calculated. The $[2\sqrt{2}/\sqrt{3} \times 4/\sqrt{3}]R35.26°$ superstructure has the lowest energy. Our search for a superstructure formation by thermal equilibration of Si adatoms confirmed this prediction.

PACS numbers: 68.20+t, 68.40.+e, 73.20.Hb, 79.70.+q

Low-energy–electron-diffraction (LEED) experiments have revealed that when a chemically reactive gas chemisorbs on a clean surface, the adlayer very often forms a superstructure.[1] Somorjai and Szalkowski,[2] and perhaps some others, believed that adatom-adatom interaction was responsible for the superstructure formation. Einstein and Schrieffer[3] proposed that the superstructure formation was due to the oscillatory nature of an "indirect" adatom-adatom interaction.[3-6] This theory, although it has been around for some years, still lacks direct experimental evidence. Field-ion-microscope (FIM) studies of adatom-adatom interactions with use of metal

TABLE I. Bonds observed out of 515 heating periods at 300 °K. Configurations refer to Figs. 1 and 2.

Configurations	Bond directions	Bond lengths	Frequencies of observation	Statistical weights	Relative binding energies
a	$\sim[1\bar{1}1]$	$\sim 2.74 \pm 0.30$ Å, or $\sim(\sqrt{3}/2)a$	28	~4	0 (reference level)
b	$[001]$	3.16 ± 0.30 Å, or $\sim a$	3	~2	−40 ± 12 meV
c	$[1\bar{1}0]$	4.47 ± 0.30 Å, or $\sim(\sqrt{2})a$	82	~2	46 ± 2 meV
d	$[1\bar{1}1]$	5.48 ± 0.30 Å, or $\sim(\sqrt{3})a$	14	~4	−18 ± 6 meV
e	$[001]$	6.32 ± 0.30 Å, or $\sim 2a$	9	~2	−11 ± 7 meV
f	$[1\bar{1}0]$	Two 4.47 ± 0.30 Å bonds	4	⋯	⋯
g	$[1\bar{1}0]$	Three 4.47 ± 0.30 Å bonds	1	⋯	⋯