Mesoscopic theory of the viscoelasticity of polymers

Shirish M. Chitanvis
*Theoretical Division, Los Alamos National Laboratory
Los Alamos, New Mexico 87545
(March 24, 2022)

Abstract

We have advanced our previous static theory of polymer entanglement involving an extended Cahn-Hilliard functional, to include time-dependent dynamics. We go beyond the Gaussian approximation, to the one-loop level, to compute the frequency dependent storage and loss moduli of the system. The three parameters in our theory are obtained by fitting to available experimental data on polystyrene melts of various chain lengths. This provides a physical representation of the parameters in terms of the chain length of the system. We discuss the importance of the various terms in our energy functional with respect to their contribution to the viscoelastic response of the polymeric system.
In a previous paper, we developed a static field theory of polymer entanglement\textsuperscript{1}, in which we introduced a non-local attractive term, in addition to the usual excluded volume term, that models resistance to the motion of polymers due to entanglement. Starting with this energy functional, we were able to use Renormalization Group techniques to describe the onset of entanglement as the average molecular weight is increased to a critical value. The onset of entanglement may be described as a cross-over phenomenon, characterized by the effective diffusion constant going to zero as the transition point is approached, thereby implying critical slowing down. We pointed out the existence of experimental evidence to support the theory.

There have been several numerical approaches developed to understand the viscoelastic response of polymers\textsuperscript{2-4}. It is of interest to see whether an alternative theory of viscoelasticity of polymers using continuum concepts can be developed. Our previous theory, being static in nature, clearly needs to be extended if one is to study the time-dependent response of polymeric systems. The chief purpose of this paper is to lay down the foundations of a time-dependent field theory of entangled polymers, primarily through a comparison with experimental results on the linear viscoelastic response of polymer melts. In future work, we shall probe the time-dependent approach to entanglement of polymeric systems, as the molecular weight is increased to a critical value. In this, we have in mind an analogy with dynamic critical phenomena, where one of the quantities of interest is the frequency dependent diffusion constant, and the manner in which it scales to zero as the transition is approached. We will also compare the results of our theory briefly to the results of the standard reptation theory approach\textsuperscript{5}.

The time-dependent internal energy functional $U$ which extends our previous static theory\textsuperscript{1} can be written down in a straightforward manner in terms of an energy density $u$:

$$
U = \int d^3s \int dt \ u(s, t)
$$

$$
\beta u = c(s, t) \frac{\partial c(s, t)}{\partial t}
$$

$$
+ \left( \frac{\alpha}{\sqrt{2}} \right) \frac{\partial c(s, t)}{\partial s_i} \frac{\partial c(s, t)}{\partial s_i}
$$

$$
+ \left( \frac{\alpha^2}{2} \right) c(s, t)c(s, t)
$$

$$
- \left( \frac{\alpha^4}{2\pi} \right) \int d^3s' c(s, t) \frac{exp(-\delta|s-s'|)}{|s-s'|} c(s', t)
$$

$$
\beta = \frac{1}{kT}
$$

(1)

where $c$ is the number concentration of the polymer strands, and $\delta^2 = \sqrt{2\alpha}$, $k$ is Boltzmann’s constant and $T$ is the temperature. This model is an extension of the standard Cahn-Hilliard approach\textsuperscript{6}. The first two terms in Eqn. (1), taken by themselves, are easily seen to lead to the time-dependent linear diffusion equation, with $\alpha$ plays a role analogous to that of a diffusion constant. The third term in the equation represents the standard excluded volume interaction. We will discuss $\alpha$ in greater detail shortly. The final non-local attractive term represents the fact that when polymers become entangled, there will be in
general a resistance to their movement. Similar approaches can be found in the literature, where authors have taken activation energies to represent entanglement. The form of our interaction term is novel, however, and we have discussed in the previous paper the rationale for choosing the parameter \(\alpha\) in the model is as given in that paper, since it leads to a number preserving Euler-Lagrange equation. It is worth noting that even standard treatments involving the excluded volume term are generally restricted to the static case, whereas we have considered here an extension to the frequency-dependent case as well.

The time and space co-ordinates in the equation are dimensionless, the scales we have chosen being \(\omega_c^{-1}\) and \(\lambda\) respectively. The dimensionless parameter \(\alpha\) can be written as \(D/\left[\lambda^2\omega_c\right]\), where \(D\) is the diffusion constant which scales as the inverse square of the molecular weight in the entangled state. Since both \(\lambda\) and \(\omega_c\) could possess a molecular weight dependence of their own, it follows that \(\alpha\) can display a dependence on molecular weight different than the scaling behavior of \(D\).

Since we wish to study polymer melts undergoing shear experiments, where they are in contact with an energy reservoir (at constant temperature), the energy which is conserved is the Helmholtz free energy \(A = U - ST\), \(S\) being the entropy and \(T\) the temperature. The entropy is given approximately as:

\[
S = \int d^3s \int dt s(s, t)
\]

\[
s(s, t) \approx c(s, t) \ln[c(s, t)]
\]

\[
(1 + c') \ln(1 + c') \approx c' + \frac{c'^2}{2} - \frac{c'^3}{6} + \frac{c'^4}{12}
\]

The last of these equations indicates an expansion around \(\lambda^{-3}\), which is identical to one in the units we have chosen. The linear terms will be ignored following convention, as they can be absorbed into the chemical potential \(\mu\), required for number conservation. In the mean field approximation, \(\mu \equiv 0\). In what follows, we shall drop the primes on the number concentration variable.

The goal of this communication is to compute the linear viscoelastic response of a polymeric system. This can be done following closely the analysis in our previous paper, to obtain an expression for the frequency dependent stress \(\sigma(\omega)\):

\[
\sigma(\omega) = -i\omega C S(k = 0, \omega) \epsilon(\omega)
\]

\[
C = \left(\frac{kT}{\omega_c\lambda^3}\right)
\]

where \(S(k, \omega)\) is the two-point correlation function for the system. Note that since we chose to take temporal Fourier transforms with respect to \(\exp(-i\omega t)\), our sign convention in the first of Eqns.(3) is opposite that in standard literature. In general \(S(k, \omega)\) is given by:

\[
S(k, \omega) = \left(S_0^{-1}(k, \omega) - \Sigma(k, \omega)\right)^{-1}
\]

\[
S_0(k, \omega) = \left(-i\omega + s_0^{-1}(k)\right)^{-1}
\]

\[
s_0(k) = \left(1 + \sqrt{2}\alpha k^2 + 2\alpha^2 k^2/(1 + \sqrt{2}k^2/\alpha)\right)^{-1} \approx \left(1 + ak^2\right)^{-1}
\]

\[
a = 2\sqrt{2}\alpha
\]
where, as usual \( \Sigma \) denotes the self-energy. From Eqn.(4), we see that \( a \) plays the role of a diffusion constant. But bearing in mind the discussion below Eqn.1, we expect its dependence on molecular weight to be different than the conventional diffusion constant \( D \), due to the manner in which we have scaled our variables.

From Eqns.(3) and (4), we see that we need to evaluate the correlation function in the long wavelength limit. We can perform this calculation using a perturbation expansion with respect to the nonlinear terms, using standard methods from field theory. These are elementary extensions of the methods detailed in Ref. 1. The vertices we obtain from Eqn.(2) are depicted in Fig.1. The diagrams which we consider are depicted in Figures 2 and 3. It is easy to show that the tadpole and bubble diagrams vanish identically and the only surviving lowest order diagram is the setting-sun diagram, whose contribution can be shown analytically to be:

\[
\Sigma_{2b}(\omega, k = 0, \omega_m) = \frac{1}{4} \int \frac{d\omega'}{2\pi} \int \frac{d^3k}{(2\pi)^3} \ S_0(k, \omega') \ S_0(k, \omega - \omega')
\]

\[
= \frac{\sqrt{i\omega - 1}}{32\pi^2a^{3/2}} \ln \left[ \frac{(\omega/2 + \omega_m)}{(\omega/2 - \omega_m)} \cdot \frac{(3\omega/2 - \omega_m)}{(3\omega/2 + \omega_m)} \right] \quad (5)
\]

Here, \( \omega \) is the frequency at which the system is being sheared. In order to obtain the final expression for the self-energy in the long wavelength limit, we first performed the frequency integral. This integral is logarithmically divergent, rendered finite through the use of a high-frequency cut-off \( \omega_m \), using the conventional procedure from field theory. \( \omega_m \) may be interpreted in the usual field-theoretic sense as an upper frequency limit below which the continuum theory is not valid. The dependence of the final answer on the cutoff \( \omega_m \) is logarithmic. Next, to perform the k-integration, we used the method of contour integration, taking care to distort the contour to avoid the branch cut implied by the logarithmic behavior of the integrand in k-space. Once this is done, it is straightforward to use the method of residues to get the expression given above. It is easy to verify that the integrand in k-space is indeed suitably convergent, and no additional cutoffs are necessary.

With Eqns.(3)-(5) in hand, we fitted experimental data on polystyrene melts characterized by a very low polydispersity, and a fairly wide range of molecular weights, ranging from just under 10\(^4\) to about 580,000. The results are encapsulated in Fig. 4. Three sets of data are shown in the figure, chosen to represent low, medium and high molecular weight samples. We have performed the fitting procedure for all the sets of data provided by Onogi et al. We have chosen to display three of the fits as being representative of the procedure. We see that the fits, while good, show signs of deteriorating slightly as the molecular weight decreases. The plateaus indicate the rubbery phase of the system. Our previous paper applies in this region. For higher frequencies (short times), the stress is much higher, which could be interpreted in terms of inertia as the system starts to be strained. For frequencies below the plateaus (long-time behavior), one might say that the polymers eventually begin to disentangle, causing the stress to start decreasing precipitously.

We began with four parameters in the theory, viz., \( \lambda, \alpha, \omega_m \) and \( \omega_c \). In performing the fitting, due to the manner in which the parameters appear in the expression for the complex modulus, it was more convenient to use the reduced set of three parameters \( C, \omega_m, a \), where \( C \) and \( a \) have both been defined earlier. While it is true that the parameters in our theory had to be chosen to get the best fit with data, we find it impressive that the function given
in Eqn.(5) is such that it provides the correct form for the storage modulus. In this manner, our theory has captured the essential aspects of the linear viscoelasticity of polymer melts. From the values obtained for the three parameters, we were able to perform a least-squares fit, yielding the following representations as functions of the molecular weight $M_n$:

\[
C \approx 3.1 \times 10^{-13} M_n^{3.7} \ (dyne \ - \ s \ - \ cm^{-2})
\]

\[
\omega_m \approx b_0 M_n^{b_1} \ (s^{-1}); \ b_0 = 0.11; \ b_1 = -1.53
\]

\[
a \approx d_0 M_n^{d_1}; \ d_0 = 0.21 \times 10^{-13}; \ d_1 = 1.35
\]

Note the scaling forms for these representations. First of all, as will be shown shortly, $C$ can be identified with the static viscosity, and we found the scaling exponent 3.7 to be reasonably close to the value of 3.4 given in the literature. To obtain this representation, it was useful to plot the fitted values of $C$ against the molecular weight $M_N$ on a log-log plot. The cut-off frequency $\omega_m$ scales inversely as approximately the $3/2$ power of the molecular weight. Finally, as advertised earlier, the dependence of $a$ on $M_n$ is different than that of the true diffusion constant $D$. The reason for this is that $a$ is proportional to $D\lambda^2\omega_c^{-1}$, which has the units of a diffusion constant, goes approximately as $\sim M_n^{-10/3}$. It is further easy to show that $\lambda \sim M_n^{-2/5}$, and $\omega_c \sim M_n^{5/2}$.

As one might perhaps expect, the entropy terms in our energy functional have a dominant effect on determining the linear viscoelastic behavior of polystyrene melts. The nonlocal attractive term, which models the resistance to the motion of entangled polymers has a less pronounced effect on linear viscoelasticity. This is consistent with our earlier calculations in the static regime, where we found that the nonlocal attractive term has a more profound effect on determining the renormalized diffusion constant than the elastic moduli. We will tackle the frequency dependence of the renormalized diffusion constant in future work.

From Fig. 4 we see that the fits to data using our theory are quite good, as are those using the standard reptation theory. The advantage of our theory is that while the reptation theory is restricted to the regime of highly entangled systems, and uses mean-field concepts, we can compute the effect of fluctuations using Feynman diagrams. With these parameteric representations, we were also able to compute the loss moduli for the samples. The curves gave a reasonable but only an average fit for the various samples. In other words, the loss moduli obtained through our procedure was not very sensitive to the parameters we obtained. Nevertheless, we note that this is an improvement over the standard reptation model approaches, which give a null loss modulus. We also went a bit further, and attempted to use the above representations to calculate the storage moduli of another polymer melt, and found reasonable agreement, suggesting that our approach has a universal flavor to it. On the other hand, the results for solid polymers were quite abysmal, indicating that our fitting procedure must be redone for non-melts. We have been unable to locate data for solid polymers or other polymer melts having the same wide scope as the results of Onogi et al. for polystyrene melts.

It is easy to show that in the zero frequency limit, the viscosity is given by:

\[
\eta = \text{Lim}_{\omega \to 0} \omega^{-1} \text{Im} \left[ -i \omega CS(k = 0, \omega) \right] \equiv C
\]

One similarly obtains an expression for the shear modulus in the zero frequency limit by considering the storage modulus. For sufficiently large values of the frequency, the experimental data show an approximately linear behavior, as does the present theory.
As mentioned at the beginning, the purpose of this note is to lay down the foundations of a time-dependent field-theoretic approach to the viscoelastic response of polymeric systems. Our eventual goal is to understand the dynamic approach to entanglement, analogous to treatments of dynamic critical phenomena.

I would like to acknowledge a useful comment by Sanat Kumar concerning the calculations. This research is supported by the Department of Energy contract W-7405-ENG-36, under the aegis of the Los Alamos National Laboratory LDRD polymer aging CD program.
REFERENCES

1 S.M. Chitanvis, Phys. Rev. E 58, 3469 (1998).
2 Y. Termonia, P. Smith, Macromolecules, 20, 835 (1987); Y. Termonia, Macromolecules, 29, 4891 (1996).
3 J. Bicerano, N.K. Grant, J.T. Seitz, K. Pant, to appear in Macromolecules (1997).
4 T. Holtzl, H.L. Trautenberg, D. Goritz, Phys. Rev. Lett., 79, 2299 (1997).
5 M. Doi, S.F. Edwards, The Theory of Polymer Dynamics, Oxford University Press, Oxford (1986).
6 J.W. Cahn and J.E. Hilliard, J. Chem. Phys., 28, 258, (1958).
7 H.B. Callen, Thermodynamics, p. 106, J. Wiley & Sons, Inc., N.Y. (1960).
8 H.J. Raveché, J. Chem. Phys. 55 2242, (1971).
9 P. Ramond, Field Theory: A Modern Primer, page 126, The Benjamin/Cummings Pub. Co., (1981).
10 J.J. Binney, N.J. Dowrick, A.J. Fisher, M.E.J. Newman, The theory of critical phenomena: An introduction to the renormalization group, Oxford Science publications, Oxford (1995).
11 S. Onogi, T. Masuda and K. Kitagawa, Macromolecules 3, 109 (1970).
12 Hohenberg PC, Halperin BI, Reviews of Modern Physics, 49, 435 (1977).
FIGURES

FIG. 1. (a) is a pictorial representation of the cubic term in $A$. Each leg corresponds to a factor of $c$, the field. The intersection of the three legs symbolizes a factor of $\gamma = 1/6$, the coupling constant. (b) is a pictorial representation of the quartic term in $A$. A factor of $-1/12$ is to be inserted at the intersection.

FIG. 2. (a) represents the tadpole diagram which is crucial in our calculations. (b) represents the setting sun diagram. Both (a) and (b) are second order contributions to the correlation function coming from the cubic interaction term, the first order corrections being null.

FIG. 3. This figure represents 1-loop (bubble) contribution from the quartic interaction term in $A$.

FIG. 4. This plot shows a comparison of our theory (solid line) with the experimental data by Onogi et al on polystyrene melts. The molecular weights are placed alongside the different sets. The comparison is fairly good, and appears to deteriorate slightly as the molecular weight decreases, indicating that the theory works better for high molecular weight melts. The plateaux indicate the rubbery regime for each sample.
Chitanvis, Fig. 1

(a)

(b)
Chitanvis, Fig. 2

(a)

(b)
Chitanvis, Fig. 3

\[(t, x) \quad (t_1, x_1) \quad (t_2, x_2) \quad (t', x')\]
