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Rotational Viscosities of Polymer Solutions in a Low Molecular Weight Nematic Liquid Crystal

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Polystyrene polymers (M.W. = 2700) were dissolved in a low molecular weight nematic mixture E63 (E. Merck) in different concentrations, and studied over a broad temperature range. The rotational viscosities, γ_1, of the mixtures were measured by using the rotating magnetic field method. Contrary to the theoretical indications and some earlier experimental results, it was found that the rotational viscosity is practically not influenced due to the polymers, which suggests that the polymer conformation is rather spherical in the anisotropic fluid. Preliminary investigations of the flow properties (capillary flow) show that the effective shear viscosity increase due to the added polymer is similar to that of isotropic solutions.

Keywords: Rotational viscosities, polymer solutions

I. INTRODUCTION

The behavior of dilute solutions of flexible polymer chains in a nematic solvent have been studied by different physical methods: neutron scattering,[1] NMR[1,2] and viscosity measurements.[3,4] We are primarily concerned with the rotational viscosity γ_1 which characterizes the friction connected with the rotation of the director field, $\mathbf{n}$, while the liquid is at rest. In many practical applications, it is necessary to optimize γ_1 to suit a particular situation, for instance; reducing the switching time in liquid crystal displays, or in controlling the drawing of high-strength fibers from liquid crystalline polymer solutions. In the latter case, γ_1 is a major factor in determining the relaxation of the director field after the fluid leaves the spinneret.[5] Furthermore, the time scale for the development of periodic or banded textures in polymeric nematics,[6] subjected to flow or magnetic fields, is essentially set by the magnitude of γ_1.

In this work we study the influence of a dissolved polymer on the rotational viscosity of a nematic liquid crystalline mixture commonly used in displays.

Previous studies measured the ratio γ_1/χ_a, (χ_a is the diamagnetic anisotropy) by

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monitoring the dynamical relaxation of the Freedericksz transition in a controlled geometry.[3] Therefore, to obtain γ_1 the values of χ_a have to be measured independently.

In this paper we report on direct γ_1 measurements of the low molecular weight nematic mixture, E63 (E. Merck, see Table I), in which different concentrations of polystyrene polymers (M.W. = 2700) were dissolved. The polystyrene could be dissolved with a concentration as high as 1.5 wt% without phase separation down to room temperatures. We could thus measure γ_1 in a broad temperature interval ($\Delta T > 60°C$). The measurements of diamagnetic anisotropies *vs* temperature and concentration were performed independently.

II. EXPERIMENTS

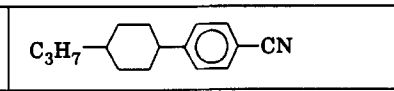
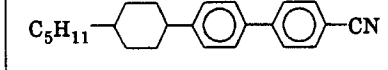
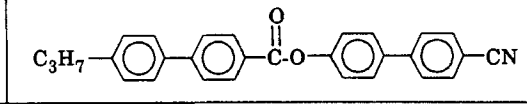
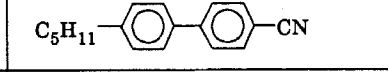
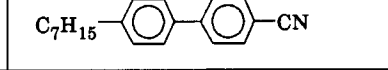
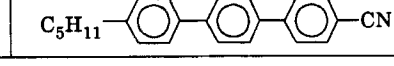
A. Rotational Viscosity Measurement

For the γ_1 measurement we use the "rotating magnetic field" method.[7-9] An NMR sample tube 5 mm in diameter and wall thickness of 0.4 mm was suspended on a 25 μm diameter tungsten wire 35 cm in length. The wire in turn was connected to a stepmotor (Oriel 20010). The step width of the rotational angle of the suspended wire was 0.01°. Applying sufficiently large magnetic fields ($H > 1$ kG) the sample was uniformly aligned, except for a very thin region, ξ, near the tube surface. [$\xi = H^{-1}(K/\chi_a)^{1/2}$ where K is an effective elastic constant.] Rotating the sample in a uniform magnetic field with angular velocity ω results in a viscous torque M which is transmitted to the torsion wire. In equilibrium we have[7]

$$M = \gamma_1 \omega \cdot V = k\alpha. \tag{1}$$

TABLE I

Components of the mixture E63

PCH3	
BICH5	
BB21	
K15	
K21	
T15	

Here α is the angular deviation of the torsion wire, and V is the sample volume $\simeq 1$ cm^3. Equation (1) is used to measure γ_1 directly. By measuring the oscillation period of a known moment of inertia, we determined the torsional constant $k = 0.17 \pm 0.005$ erg. This value held for all investigated temperatures.

For the determination of the torsion angles a small mirror was attached to the bottom of the wire above the sample tube. It reflected a laser beam onto a photodiode. When the light intensity measured by the photodiode was larger than a selected threshold, a computer read the position of the stepmotor. The program controlling the measurement checked the signal of photodiode every 15 milliseconds.

The primary systematic source of error was a lack of rotational symmetry of the sample tubes. The magnetization of the tube in a homogeneous magnetic field is $m_i = K_{ij}H_j$. We are interested in the horizontal part of the magnetization and may write for the angular dependence of the magnetic energy of the tube.

$$F_t = -\frac{1}{2} K_t H^2 \cos^2\beta_t$$

where β_t is the angle between the magnetic field and an axis of the susceptibility tensor, and K_t is the volumetric susceptibility anisotropy of the tube. For the tube used in these measurements $K_t \simeq 3.1 \times 10^{-10}$ cgs. This value was determined from the maximum deflection angle when the magnetic field was switched from 0 to 10 kG. The deflection angle did not change significantly (<0.01 rad) when the same experiment was performed with the isotropic phase of the sample (volume $\simeq$1 cm^3) in the tube. This indicates the form anisotropy of the sample volume was negligible. The anisotropy of the mirror and cap were also negligible. The main contribution to the anisotropy of the tube was therefore due to variations in wall thickness, and, or lack of concentricity of the inner and outer diameters.

For the experiment we found it convenient to mark the position of the anisotropy axis of the tube relative to the cap (mirror). We found that the errors involved in repositioning the tube to the mark were negligible.

The anisotropy of the sample tube causes a non-uniform rotation even after the decay of any transient oscillations. In a first approximation, it causes a superimposed pulsation at a frequency 2ω, where ω is the frequency of the stepmotor rotation. In order to reduce the error, we measured the torsion angle at a rotation speed $\omega = 0.1787$ rad/sec (α_1), and at half this speed (α_2). We then used the relation $\gamma_1 = 2k(\alpha_1 - \alpha_2)/\omega$. (We have verified that α is linear in ω over the range of speeds used in this experiment.) The effect of the tube anisotropy thus cancels in the difference $\alpha_1 - \alpha_2$. This procedure is effective as long as the inertial terms can be neglected, i.e., from Equation (4); $\ddot{\alpha} << \omega_0^2\alpha$. For the parameters of our experiment this was true for $\gamma_1 > 0.1$ poise. The experiment was done for both clockwise and counterclockwise rotations with no significant difference detected.

The bottom of the sample was thermostatted to the accuracy of 0.01°C. The temperature differences between the top and the bottom of the samples were less than 0.1°C over the range of temperatures scanned. As a check of the apparatus we measured γ_1 of MBBA (new). Our values of γ_1 match (within 1.4%) published values for this material[8] for all temperatures accessible to our instrument.

B. Investigation of the Flow Properties

As a simple comparison, solutions with different concentrations of polymer were placed in same size pipettes and the efflux times, t, were compared to the efflux time of the solvent, t_o. In this way we obtained the relative viscosity, $\eta_r = t/t_o$. The flow rate was slow enough to neglect kinetic corrections.

C. Measurement of the Diamagnetic Anisotropies

The diamagnetic anisotropy was determined from the change in the torsional oscillation frequencies of the sample in different magnetic fields. In Reference (10), this method was used in the case of lyotropic liquid crystals, where γ_1 is much larger and χ_a is much smaller than in thermotropics. However this method, when suitably extended, is also applicable to determine χ_a in thermotropics.

The assumptions made in the following are: i) The liquid and the sample tube rotate as a rigid body. This requires the Reynold number, $Re = v_o R/\nu << 1$ (v_o is a typical velocity, R is the tube radius and ν is a kinematic shear viscosity). We estimate $Re < 10^{-1}$ in our measurement. ii) The director field is uniformly aligned by the applied magnetic field, H; this means $\xi << R$. With these assumptions the equations governing the director motion and the motion of the torsion pendulum can be written

$$\dot{\beta} + \dot{\alpha} = \dot{\theta} + \frac{1}{2\tau} \sin 2\theta, \tag{3}$$

$$\ddot{\beta} + \ddot{\alpha} = -\omega_o^2 \left\{ \alpha + \frac{\kappa}{2} \sin 2\theta + \frac{\kappa_t}{2} \sin 2(\alpha + \beta) \right\}, \tag{4}$$

where

$$\omega_o^2 = k/I, \quad \tau = \gamma_1/\chi_a H^2, \quad \kappa = \chi_a H^2 V/k, \quad \kappa_t = K_t H^2/k. \tag{5}$$

Here I is the inertial moment of the pendulum, θ is the angle between H and the director field, and β is the angular position of the stepper motor. The stepper motor position remains fixed during this experiment so $\dot{\beta}$ and $\ddot{\beta}$ are zero. If we neglect the anisotropy of the tube, $\kappa_t/\kappa << 1$, and assume a small oscillation amplitude, writing $\sin\theta \simeq \theta$, the solution follows (see Appendix),

$$a(t) \sim \alpha_o \exp(-\Gamma t) \sin \Omega t. \tag{6}$$

Expressions for the magnetic field dependence of Ω and Γ are given in the Appendix. When $\omega_o \tau >> 1$ these expressions reduce to those derived in Reference (10). When $\omega_o \tau > 1$ we obtain χ_a from the temperature behavior of γ_1 (found independently), and the measured values of Ω *vs* temperature at constant H.

The error in measuring χ_a is about 10%. This error is largely due to the damping,

which allowed only a small number (~5–10) of oscillations to determine Ω. The error caused by the tube anisotropy can be estimated from Equation (4). For α small the natural oscillation frequency is shifted to $\tilde{\omega}_o \cong \omega_o(1 + 1/2\ \kappa_t \cos 2\beta) \simeq \omega_o(1 \pm 0.005)$, for $H = 2$ kG. This is the maximum shift if β was not adjusted to reduce the initial torsion on the wire. If $\beta \simeq \pi/4$ the shift of ω_o vanishes in the first approximation ($\alpha << 1$). We conclude the error in χ_a was mostly due to visual counting of the oscillations.

III. SAMPLES

The solvent used is a liquid crystal mixture E63 produced by E. Merck. We dissolved polystyrene, M.W. = 2700 (Aldrich Chemical Co.) into E63 in concentrations of 0.5%, 1.0% and 1.5% wt%. The solution was mixed before and after pipetting into the NMR tube and examined for homogeneity. In every case the measurements started at room temperature, then gradually heating the sample to the isotropic phase. Measurements were also taken on cooling, but concentration gradients arose if the sample was left in the two-phase region too long.

For evaluation of the temperature behavior of the mixtures we used the following:

- T_N^+: the temperature at which the first isotropic drop appears when heating.
- T_N^-: the temperature where the isotropic phase completely disappears when cooling.
- T_I^-: the temperature where the nematic phase begins to appear in cooling.

The transition temperatures were investigated by polarizing microscope, and in bulk using a stirred water bath. The accuracy is ±1°C. In both cases the above defined temperatures T_N^+, T_N^- and T_I^- were found to be approximately the same. The averaged phase transition temperatures are summarized in Table II. The trends in the transition temperatures *vs* concentration are similar to those measured in Reference (3), except that in our case at high temperature the solvent itself has a two-phase region. Phase separation was not evident down to room temperature.

IV. EXPERIMENTAL RESULTS

A. Rotational Viscosities

In Figure (1), γ_1 is plotted *vs* temperature. There does not appear to be any systematic trend of γ_1 with polymer concentration. In all the figures the symbol sizes give the approximate measuring errors.

TABLE II

Sample compositions and transition temperatures

Mixture wt%	T_N^+ (°C)	T_I^- (°C)	T_N^- (°C)
E63+0.0%	88.5	90.0	88
E63+0.5%	85	88	78
E63+1.0%	78	87	69
E63+1.5%	71	78	56

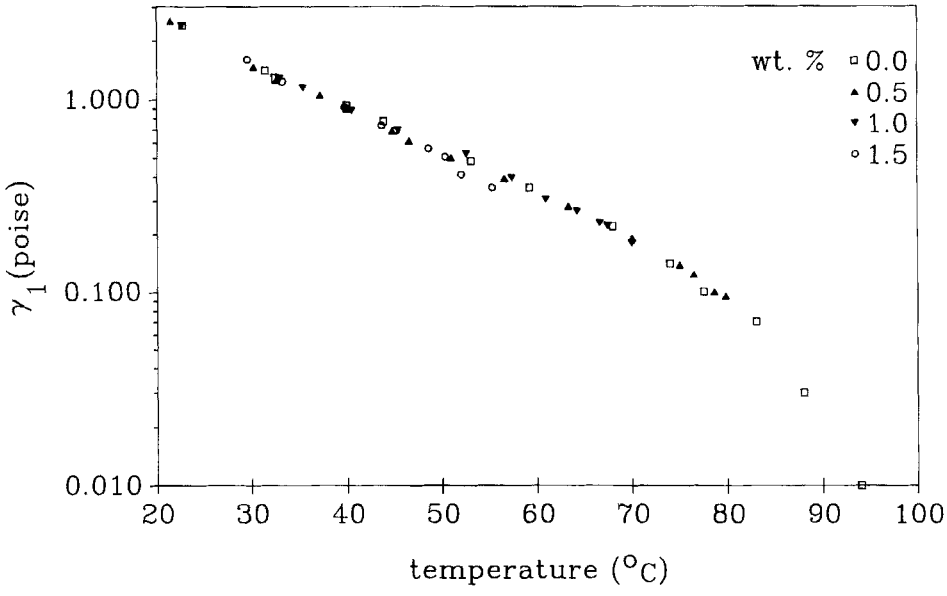


FIGURE 1 Temperature dependencies of rotational viscosities of different concentration solutions of polystyrene (M.W. = 2700) in the nematic phase of E63.

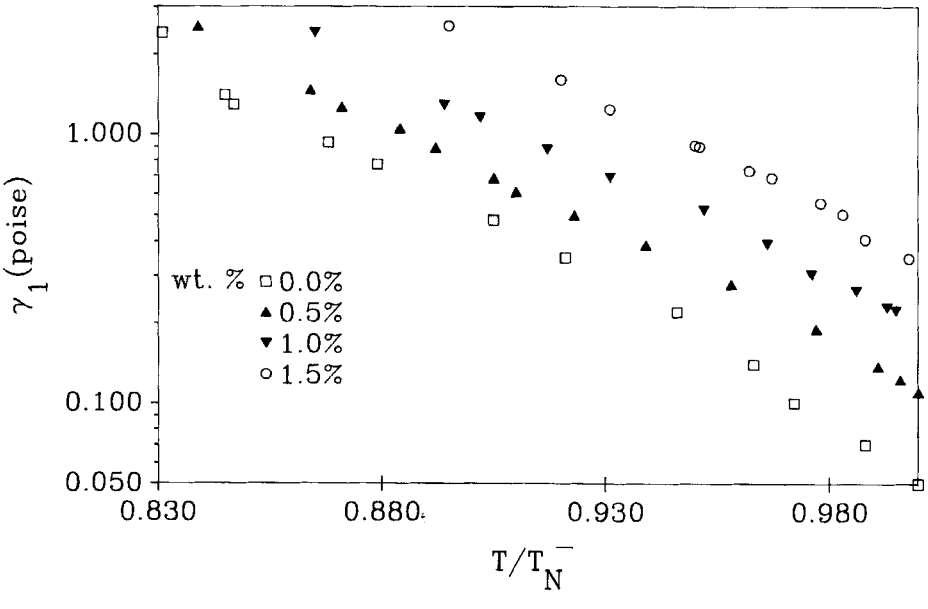


FIGURE 2 Rotational viscosities *vs* the relative temperature $T/T_{\bar{N}}$ in case of different concentrations of PS2700 dissolved in E63.

In Figure (2) we plotted γ_1 *vs* reduced temperature. Using this scale it appears that there is a systematic increase of γ_1 with polymer concentration. This is mostly caused, however, by the increase of the background solvent viscosity due to the downward shift of the phase transition temperatures.

B. Relative Shear Viscosities

As mentioned above, our preliminary measurements of the relative shear viscosities η_r at room temperature yield,

$$\eta_r(1.5\%\ \text{PS}) = 1.25 \pm 0.03 \text{ and } \eta_r(1.0\%\ \text{PS}) = 1.11 \pm 0.03.$$

These should not change significantly through the nematic phase. The trends are similar to those found by Martinoty[4] for an isotropic solution of polystyrene (1.7 wt%, M.W. = 2100) in dibutylphtalate where $\eta_r \simeq 1.2$ ($T = 50°C$) and the nematic EBBA (*p*-ethoxybenzylidene-*p*-*n*-butylaniline) + 1.7 wt% PS2100, where $\eta_r \simeq 2.0$ ($T = 50°C$).

C. Diamagnetic Anisotropies

The diamagnetic anisotropies as a function of temperature are presented in Figure (3). As expected the magnitudes of the diamagnetic anisotropies of all the solutions were the same within the measuring error. However, the jump in χ_a at $T_{\bar{N}}$ appears to increase with increasing polymer concentration.

V. DISCUSSION AND CONCLUSIONS

A. Temperature Dependences

The temperature dependence of γ_1 can be analyzed by the equation[11,12]:

$$\gamma_1 = B \cdot S^a \cdot \exp(E_a/(T - T_o)) \tag{7}$$

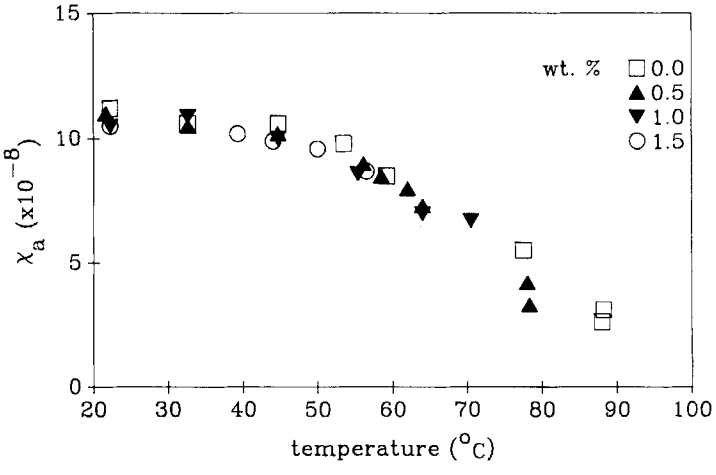


FIGURE 3 Diamagnetic anisotropies (in cgs) of E63 and three different solutions of PS2700 dissolved in E63. The vertical dashed lines indicate the phase transition temperatures $T_{\bar{N}}$.

In order to compare our results to models based on Equation (7), we need to know the temperature dependence of the order parameter. Different values of a ($= 1,2$) are found by different authors.[11,12] To choose between these we plotted γ_1/S and γ_1/S^2. We used the fact that χ_a is proportional to S. The proportionality coefficient was chosen such that at room temperature (which is about 60°C below the phase transition temperature T_N^-) $S \simeq 0.8$. In Figures (4a b) $\ln(\gamma_1/S)$ and $\ln(\gamma_1/S^2)$ are presented *vs* the inverse temperature. For our system it appears γ_1 is proportional to S, corresponding to the results of Prost at al.[11]

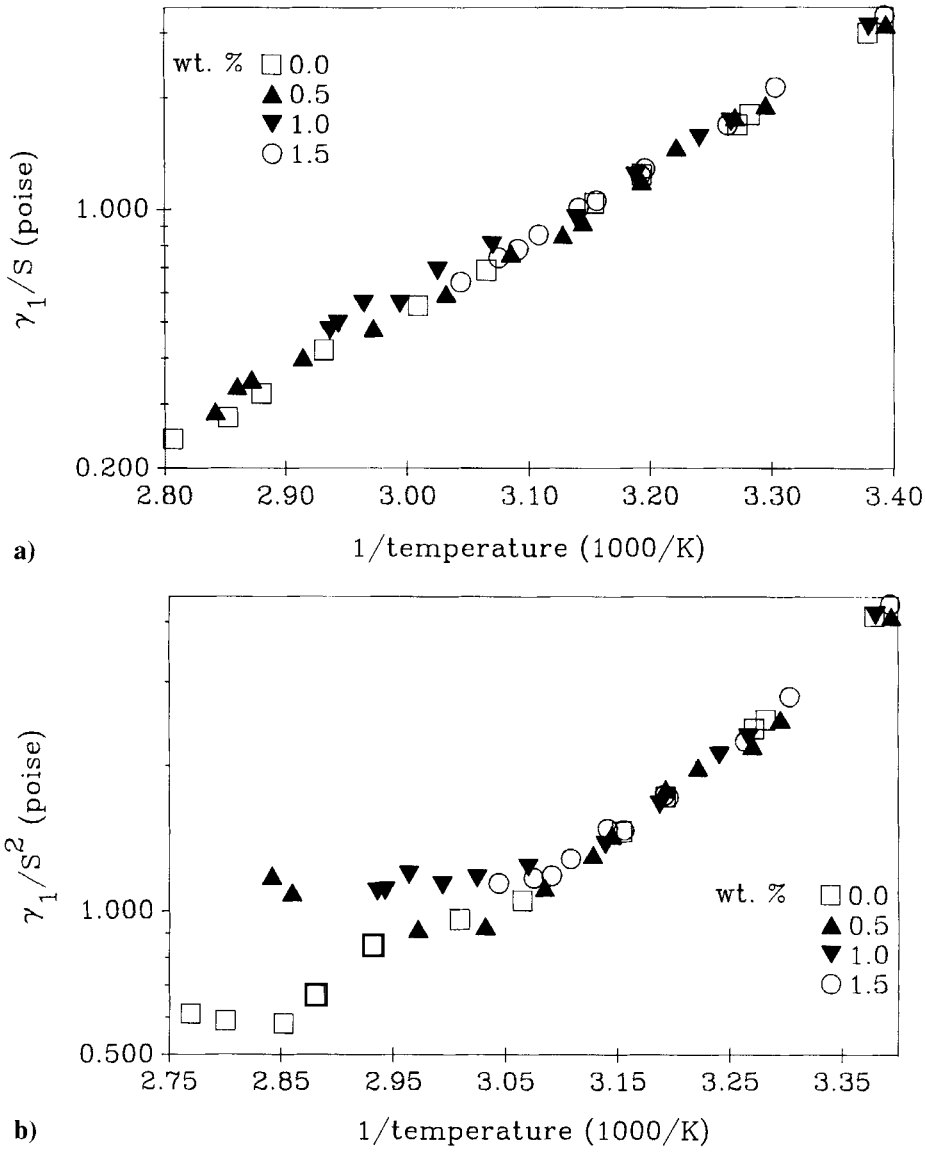


FIGURE 4 Determination of the order parameter (S) dependence of the rotational viscosities of E63 + PS2700 mixtures; a) γ_1/S vs. $1000/T(K)$; b) γ_1/S^2 vs. $1000/T(K)$.

B. Concentration Dependence

We find: a) On the absolute temperature scale the rotational viscosity, γ_1, is practically unaffected by addition of the polymer. b) The relative shear viscosity increases in a manner consistent with classical isotropic solutions.[13]

The first conclusion appears to be in conflict with theoretical[14] and earlier experimental results[3] on dissolved polymers in nematics. The theoretical work of Brochard indicates the coil must have an anisotropic configuration in order to affect γ_1. Interpreting our results in this light would imply the polymer configurations, in our samples, are roughly spherical on the average. Experimentally, we must note that the previous work[3] used pure nematic solvents, whereas we used a five-component mixture as the solvent. Studies are in progress to establish if this difference is important.

Acknowledgment

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APPENDIX

Here we sketch the solution to Equations (3) and (4). Let

$$\alpha = \alpha_o e^{\sigma\tau}, \ \theta = \theta_o e^{\sigma\tau}. \tag{A1}$$

Substituting in Equations (3) and (4), and eliminating θ we obtain the equation for $x = \sigma\tau$,

$$x^3 + x^2 + (\omega\tau)^2 x + (\omega_o\tau)^2 = 0 \tag{A2}$$

where $\tau = \gamma_1/\chi_a H^2$, $\omega_o^2 = k/I$ and $\omega = \omega_o(1 + \kappa)^{1/2}$.

Equation (A2) yields one negative real root, σ_1, corresponding to a pure damping with no oscillations and two complex roots, $\sigma_{2,3} = -\Gamma \pm i\Omega$ with angular frequency

$$\Omega = \frac{\sqrt{3}}{2\tau}(u - v) \tag{A3}$$

and damping rate

$$\Gamma = \frac{1}{2\tau}(u + v) + \frac{1}{3\tau}. \tag{A4}$$

Where

$$\begin{Bmatrix} u \\ v \end{Bmatrix} = (-q \pm (q^2 + p^3)^{1/2})^{1/3} \tag{A5}$$

and

$$q = \frac{1}{27} - \frac{(\omega\tau)^2}{6} + \frac{(\omega_o\tau)^2}{2} \tag{A6}$$

$$p = \frac{(\omega\tau)^2}{3} - \frac{1}{9}.$$

In the limit $\omega_o\tau >> 1$ we find,

$$\Omega \simeq \omega = \omega_o(1 + \kappa)^{1/2} \tag{A7}$$

and

$$\Gamma \simeq \frac{\kappa}{2\tau(1 + \kappa)}, \tag{A8}$$

in agreement with the expressions used in Reference (10). When necessary, (i.e., when $\omega_o\tau \sim 1$) we use Equations (A3), (A5), (A6), along with the previously found $\gamma_1(T)$ to reduce the systematic numerical error in determining χ_a.

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