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DYNAMIC SUSCEPTIBILITY OF A MODEL POLYMER IN SEVERAL LIMITS --

THEORY AND CALCULATIONS.

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Abstract

We study the susceptibility of a model polymer having
rotating dipolar sidechains with nearest neighbor interactions
and diagonal viscosity. The susceptibility can be found
exactly (1) at zero frequency for arbitrary interaction strength,
and (2) at zero interaction strength for arbitrary frequency
and viscosity. In addition, a high-temperature expansion exists
for arbitrary frequency both in the viscous limit and for finite
viscosity. We also study the time-dependent correlation function
$< \cos \varphi_i(t) \cos \varphi_{i+1}(0) >$ for arbitrary viscosity and weak
interaction, and the possibility of a more complex diagonal
friction law. In no case are we able to produce a Cole-Cole
plot which approaches the origin with finite slope at high
frequencies, as does much experimental data.

I. Introduction

There has been some interest in recent years in the dynamical (nonequilibrium) properties of many-particle systems under the influence of stochastic forces. Examples include the work of Glauber on the Ising model[1], and a series of papers on harmonic oscillator systems by Oppenheim, Shuler and Weiss.[2]

Various properties of polymers have been considered candidates for explanation by such models.[3,4,5] In this paper we study a model similar to that proposed by Work and Fujita[6] to explain dielectric relaxation in certain polymers. The frequency dependent susceptibility of such polymers, as represented on a Cole-Cole plot, takes either the semicircular Debye form $(1-i\omega\tau)^{-1}$, or a distorted form which approaches the origin with finite slope (Fig. 1.).[7]

Our model is a polymer consisting of a backbone with polar sidechains free to rotate in the plane normal to the backbone. Each such side element has a dipole moment μ (which we henceforth set to unity) and is subject to a random torque. We furthermore suppose an interaction between nearest neighbors of the form $v \cos(\varphi_i - \varphi_{i-1})$, so as to create a tendency toward antiferroelectric alignment for $v > 0$. (This would be an excellent approximation if the interaction is electrostatic in origin, taking $v \sim \mu^2/a^3$, with a the nearest neighbor distance. However, it is rather naive to suppose this to be the case.)

We then attempt to calculate the linear susceptibility for arbitrary frequency.

In section II we present the solution of the model for zero frequency. Section III reviews the theory of motion in the field of a random force. In section IV we derive a high-temperature expansion for the susceptibility in the viscous limit. In section V we derive the susceptibility for the noninteracting system in the case of finite viscosity, and we demonstrate the existence of a high-temperature expansion. Section VI deals with the dynamic, linear nearest-neighbor correlation function for the case of finite viscosity. Section VII discusses the case of a more complex random force, and we summarize our conclusions in section VIII.

In all the cases we consider we are unable to convincingly produce a Cole-Cole plot which approaches the origin with finite slope as in Figure 1. This suggests that our model, as well as all similar models, lacks the essential ingredient needed to produce such behavior.

II. Exact Equilibrium Results

At equilibrium it is possible to find many properties exactly by the techniques used by Fisher[8] on the classical Heisenberg model. We give these calculations in some detail both for completeness and because we will use some of the results later.

The Hamiltonian is given by

$$H = H_k + H_v + H_E(t) \tag{1}$$

where

$$H_k = \frac{1}{2I} \sum_j p_j^2$$

$$H_E = -E \sum_j \cos (\varphi_j - \omega t) \tag{2}$$

$$H_v = v \sum_j \cos (\varphi_j - \varphi_{j-1}) \quad,$$

we use I to denote the moment of inertia per sidechain, and p_j is the momentum conjugate to the angular position φ_j. The partition function (for $\omega = 0$) is then

$$Z = \left[\prod_j \int dp_j \exp\left(- \frac{\beta}{2I} p_j^2 \right)\right]\left[\int d^N\varphi_j \exp(-\beta\sum_j (v \cos u_j - E \cos \varphi_j)\right] \tag{3}$$

where we have written $u_j = \varphi_j - \varphi_{j-1}$. At zero applied field, and neglecting end effects, the partition function may be evaluated to give

$$Z = (2\pi I T)^{-N/2} (2\pi I_0(v/T))^N \tag{4}$$

where I_o is the Bessel function for imaginary argument, and we have set Boltzmann's constant to unity. This result enables the calculation of such thermal properties as the specific heat by the usual methods. (See Fig. 2).

Next we calculate the correlation function

$$< \exp[i(\varphi_o - \varphi_k)] > = 2< \cos \varphi_o \cos \varphi_k >$$

$$= 2< \sin \varphi_o \sin \varphi_k > . \tag{5}$$

For concreteness we take $k > 0$. We note that

$$\cos \varphi_k = \cos(u_k + \varphi_{k-1}) = \cos u_k \cos \varphi_{k-1} - \sin u_k \sin \varphi_{k-1} . \tag{6}$$

Thus

$$< \cos \varphi_o \cos \varphi_k > = \frac{1}{Z} \int d\varphi_o \cos \varphi_o \int d^{N-1} u \cos \varphi_k \exp(-\beta v \sum_k \cos u_k)$$

$$= \frac{1}{Z} \int d\varphi_o \cos \varphi_o \int d^{N-1} u (\cos u_k \cos \varphi_{k-1} - \sin u_k \sin \varphi_{k-1}) \tag{7}$$

where we use the fact that there are N variables φ, but only $N-1$ variables u. Since the u_ks are all independent, and since $< \sin u_k > = 0$, we get a recursion formula

$$< \cos \varphi_o \cos \varphi_k > = < \cos u_k >< \cos \varphi_o \cos \varphi_{k-1} > . \tag{8}$$

Now,

$$< \cos u_j > = - \frac{\partial}{\partial(\beta v)} \ell n \int du_j \exp(-\beta v \cos u_j)$$

$$= -I_o'(\beta v)/I_o(\beta v) \tag{9}$$

and $< \cos^2 \varphi_o > = \frac{1}{2}$, so that

$$< \exp[i(\varphi_o - \varphi_k)] > = [-I_o'(\beta v)/I_o(\beta v)]^k . \tag{10}$$

The function $< -e^{i(\varphi_o - \varphi_1)} > = I_o'/I_o$ is shown on Figure 2.

Furthermore, we may calculate

$$
\begin{aligned}
< \exp[2i(\varphi_o - \varphi_1)] > &= < \cos 2u_1 > \\
&= < 2\cos^2 u_1 - 1 > \\
&= [2I_o''(\beta v) - I_o(\beta v)]/I_o(\beta v) \tag{11}
\end{aligned}
$$

and this technique may be extended to $< e^{in(\varphi_o - \varphi_1)} >$.

Finally, using once again the independence of the coordinates u_i, we may calculate such a term as

$$< \exp\left[i \sum_{j=0}^{k} n_j \varphi_j\right] > = < \exp[in_k u_k] > < \exp[i(n_{k-1} - n_k)\varphi_{k-1} + i \sum_{j=0}^{k-2} \varphi_j] > \tag{12}$$

Since all coordinates u_i are independent.

The static susceptibility is given by

$$\chi = \beta \sum_{ij} < \cos \varphi_i \cos \varphi_j > \tag{13}$$

which can be derived by differentiating the partition function twice with respect to E before taking the zero-field limit. This is easily evaluated to give

$$
\begin{aligned}
\chi &= \frac{N\beta}{2}\left(1 + 2 \sum_{k=1}^{\infty} \left[-\frac{I_o'(\beta v)}{I_o(\beta v)}\right]^k\right) \\
&= \left(\frac{N}{2T}\right)\left(\frac{I_o(\beta v) - I_o'(\beta v)}{I_o(\beta v) + I_o'(\beta v)}\right) \tag{14}
\end{aligned}
$$

$$\chi \xrightarrow[\beta v \to \infty]{} \left(\frac{N}{2T}\right) \frac{T}{4v} = \frac{N}{8v} . \tag{15}$$

III. Review of the Theory of a Particle Subject to a Random Force

In this section we outline the theory of a system subject to a random force in order to derive the equations basic to subsequent sections. We follow the development of Kramers.[9]

An ensemble of model polymers may be characterized by a distribution function $\rho(\underline{\varphi}, \underline{p}, t)$, where $\underline{\varphi}$ and $\underline{p}$ are N-dimensional vectors describing the angular positions and momenta of the side-chains of a given polymer. We wish to calculate

$$\frac{\partial \rho}{\partial t} \approx \frac{1}{\tau} \left\{ \rho(\underline{\varphi}, \underline{p}, t + \tau) - \rho(\underline{\varphi}, \underline{p}, t) \right\} \tag{16}$$

where τ is a macroscopically small time interval. We proceed using

$$\underline{\dot{\varphi}} = \frac{1}{I} \underline{p} \tag{17a}$$

and

$$\underline{\dot{p}} = -\nabla_{\underline{\varphi}} U(\underline{\varphi}) + \frac{1}{\tau} \underline{B}_\tau \tag{17b}$$

where

$$\underline{B}_\tau = \int_t^{t+\tau} \underline{X}(t) dt \tag{18}$$

$X_i(t)$ being the random torque on the ith sidechain, and $\underline{B}_\tau$ is described by a distribution $\Phi_\tau(\underline{B}, \underline{\varphi}, \underline{p})$. Then

$$\rho(\underline{\varphi}, \underline{p}, t + \tau) = \int d^N B \rho(\underline{\varphi} - \frac{\tau}{I}\underline{p}, \underline{p} + \tau\nabla_{\underline{\varphi}}U(\underline{\varphi}) - \underline{B}, t)\Phi_\tau(\underline{B}, \underline{\varphi}, \underline{p}) \tag{19}$$

which leads to

$$\frac{\partial \rho}{\partial t} \approx -\frac{1}{I}\underline{p} \cdot \nabla_{\underline{\varphi}} \rho + \nabla_{\underline{\varphi}}U(\underline{\varphi}) \cdot \nabla_{\underline{p}} \rho + \frac{1}{\tau} \Delta\rho \tag{20}$$

where

$$\Delta\rho = \int d^N B [\rho(\underline{\varphi}, \underline{p} - \underline{B}, t) - \rho(\underline{\varphi}, \underline{p}, t)]\Phi_\tau(\underline{B}, \underline{\varphi}, \underline{p})$$

$$= \sum_i \int_{-\infty}^{\infty} dB_i \left\{ \sum_{m=1}^{\infty} \frac{(-B_i)^m}{m!} \left(\frac{\partial}{\partial p_i} \right)^m (\rho \Phi) \right\} \quad . \tag{21}$$

Note that we have assumed the random forces on different side-chains to be uncorrelated, and also that Φ_τ is independent of $\underline{\phi}$. Defining

$$\mu_n = \int_{-\infty}^{\infty} B^n \Phi(B,p) dB \tag{22}$$

yields the Fokker-Planck equation

$$\frac{\partial \rho}{\partial t} = \nabla_{\underline{\phi}} U(\phi) \cdot \nabla_{\underline{p}} \rho - \underline{p} \cdot \nabla_{\underline{\phi}} \rho + \sum_i \sum_{n=1}^{\infty} \frac{1}{n!} \left(- \frac{\partial}{\partial p_i} \right)^n \left(\frac{\mu_n}{\tau} \rho \right) \tag{23}$$

It is usual to choose (Einstein damping) $\mu_1 = -\eta p \tau$, $\mu_2 = 2\eta I T \tau$, and all higher moments zero. This choice is not unique, however. The moments μ_i are restricted only by the conditions that the Maxwell-Boltzmann distribution be stationary and stable. We shall return to this point in section VII. Under the usual choice of μ_i, (23) becomes

$$\frac{\partial \rho}{\partial t} = \nabla_{\underline{\phi}} U(\phi) \cdot \nabla_{\underline{p}} \rho - \underline{p} \cdot \nabla_{\underline{\phi}} \rho + \eta \nabla_{\underline{p}} \cdot (\underline{p} \rho + I T \nabla_{\underline{p}} \rho) \quad . \tag{24}$$

In the case of large viscosity, it is customary to assume that

$$\rho(\underline{\phi}, \underline{p}, t) = \sigma(\underline{\phi}, t) \exp[-\underline{p} \cdot \underline{p}/2IT] \tag{25}$$

The equation for σ is derived by integrating (24) over the path $\underline{\phi} + \underline{p}/\eta I = \underline{\phi}_o$ from $p_i = -\infty$ to $+\infty$, and assuming that the force and the distribution $\rho(\underline{\phi}, \underline{p})$ have nearly the same values as at ϕ_o over the region making the main contribution to the

integral. This leads to the diffusion equation

$$I\eta \frac{\partial \sigma}{\partial t} = \underline{\nabla}_{\varphi} \cdot [(\underline{\nabla}_{\varphi} U(\underline{\varphi}))\sigma + T\underline{\nabla}_{\varphi}\sigma].$$ (26)

IV. Susceptibility in the Viscous Limit

1. Single Particle Susceptibility

In this subsection we calculate the susceptibility of an ensemble of noninteracting side-chains whose dynamics are governed by equation (26), with $U = -E \cos \theta$, $\theta = \varphi - \omega t$. The quantity we will calculate is a reduced susceptibility given by

$$\chi = 2T \frac{\partial}{\partial E} < e^{-i\theta} > \tag{27}$$

We will write (26) in the form

$$\frac{I\eta}{T} \frac{\partial \sigma}{\partial t} = \frac{E}{T} \frac{\partial}{\partial \varphi}(\sigma \sin(\varphi - \omega t)) + \frac{\partial^2 \sigma}{\partial \varphi^2} \tag{28}$$

Denoting $I\eta/T$ by τ_1 and writing

$$\sigma(\varphi, t) = \frac{1}{2\pi} \sum_{n=-\infty}^{\infty} A_n e^{in\theta} \tag{29}$$

gives

$$\sum_n (n^2 - inz)A_n = iy \frac{\partial}{\partial \theta}[(e^{i\theta} - e^{-i\theta}) \sum_n A_n e^{in\theta}] \tag{30}$$

where $z = \omega \tau_1$ and $y = E/2T$. Equating powers of $e^{i\theta}$ gives

$$(n - iz) A_n = y(A_{n-1} - A_{n+1}) . \tag{31}$$

Now we observe that, using $A_o = 1$,

$$< e^{-i\theta} > = A_1 = \frac{y}{1-iz} + O(y^3). \tag{32}$$

This yields, then, the expected result

$$\chi = (1 - iz)^{-1}. \tag{33}$$

2. Many Particle Susceptibility

For our model we need consider a distribution function

$$\sigma = \sigma(\varphi_1, \ldots, \varphi_N, t) \tag{34}$$

with a potential given by $H_E + H_v$. The generalization of equation (29) is

$$\sigma = \left(\frac{1}{2\pi}\right)^N \sum_{\{n_j\}} A_{\{n_j\}} \exp(i\sum_j n_j \theta_j); \qquad A_{\{0\}} = 1. \qquad (35)$$

We assume that (a) $A_{\{n_j\}}$ is invariant under $j \to j + m$ or $j \to m - j$; (b) we may neglect $A_{\{n_j\}}$ if more than a few nearby n_j's are nonzero, provided v/T is not too large; and (c) end effects are negligible. Under these assumptions, we may write the generalization of equation (31) as

$$\left(\sum_j n_j^2 - iz \sum_j n_j\right) A_{\{n_j\}} = y \sum_j n_j (A_{\ldots,n_{j-1},n_j-1,n_{j+1},\ldots} \\ - A_{\ldots,n_{j-1},n_j+1,n_{j+1},\ldots})$$

$$(36)$$

$$\ominus x\sum_j n_j (A_{\ldots n_j-1,n_{j+1}+1,\ldots} + A_{\ldots n_{j-1}+1,n_j-1,\ldots} \\ - A_{\ldots,n_j+1,n_{j+1}-1,\ldots} - A_{\ldots n_{j-1}-1,n_j+1,\ldots})$$

where $x = v/2T$.

For simplicity, in what follows we subscript the coefficients A only with indices from the region in which they may be nonzero, such a procedure being justified by the assumptions (a, b, c) above. Once again, our object is to find the coefficient A_1 to linear order in y, but as a power series in x. The equation for A_1 is now

$$(1 - iz)A_1 = y(A_o - A_2) - 2x(A_1 - A_{2,-1}). \qquad (37)$$

Since $A_2 \sim y^2$ and $A_{2,-1} \sim xy$, we have, to linear order in x,

$$A_1 = \frac{y}{1 + 2x - iz} . \tag{38}$$

To go to higher order in x we must write the equation for $A_{2,-1}$, which is

$$(5 - iz)A_{2,-1} = y(2A_{1,-1} - 2A_{3,-1} - S_{2,-2} + A_2)$$
$$-x(3A_1 - 3A_{3,-2} + 2A_{1,1,-1} - 2A_{-1,3,-1}$$
$$-A_{2,-2,1} + A_{2,0,-1}). \tag{39}$$

Four types of quantities appear on the right handside: (1) A_1 appears in a previous equation, and may be handled algebraically or expanded to low order; (2) A_2 and $A_{3,-1}$ are proportional to y^2 and may be ignored; (3) $A_{1,-1}$ and $A_{2,-2}$ are known from the exact results of section II, or, alternatively, may be expanded as a power series using (36); (4) The remaining terms satisfy equations similar to (39), and contribute to the susceptibility terms cubic or higher in x. We may thus proceed to include terms to arbitrarily high powers of $x = v/2T$. Including terms through x^5 leads to the Cole-Cole plots shown in Figure 3.

For the highest values we have plotted ($x = 0.6$ and $x = 1.0$) the Cole-Cole plot is definitely distorted from a semi-circular shape, showing some tendency toward the plot of Figure 1. (See Figure 4.)

The numerical results suggest that, for very high frequencies $z \gg (1 + 8x)$, the susceptibility may be well fit by

$$\chi''(z) = z^{-1}$$

$$\chi'(z) = (1 + 5.2x^{4/3})z^{-2} \tag{40}$$

for $0 < x < 3$. The slope of the resulting Cole-Cole plot, $\chi''/\chi' \sim zx^{-4/3}$ is less than that of the semicircle $(\alpha x - iz)^{-1}$, for which $\chi''/\chi' \sim zx^{-1}$.

V. Susceptibility in the Finite Viscosity Case

1. Single Particle

To find the susceptibility when the approximations leading to (26) do not apply, it is necessary to deal with the Fokker-Planck equation (24),[10] which for our case becomes

$$\frac{\partial \rho}{\partial t} = E \sin(\varphi - \omega t) \frac{\partial \rho}{\partial p} - p \frac{\partial \rho}{\partial \varphi} + \eta \frac{\partial}{\partial p}\left(p\rho + IT \frac{\partial \rho}{\partial p}\right) \qquad (41)$$

We define $g(\theta, p) = (\varphi, p, \frac{\varphi - \theta}{\omega}) \exp(p^2/2IT)$, and its fourier transform $g(n,p)$ by

$$g(\theta,p) = (2\pi)^{-1} \sum_{n} e^{in\theta} g(n,p). \qquad (42)$$

The susceptibility is now given by

$$\chi \equiv 2T \frac{\partial}{\partial E} < e^{-i\theta} > = (2\pi IT)^{-\frac{1}{2}} \int dp \, \exp(-p^2/2IT) f_o (p^2/IT)^{\frac{1}{2}} \qquad (43)$$

where $f_o (p^2/IT)^{\frac{1}{2}} = g(1,p)$ evaluated at $E/2T = 1$ (keeping only terms linear in E), and satisfies the equation

$$[L(x) + i(\omega\tau_2 - x(\tau_2/\tau_1)^{\frac{1}{2}})]f_o(x) = -ix(\tau_2/\tau_1)^{\frac{1}{2}}. \qquad (44)$$

Here we have defined $\tau_2 = \eta^{-1}$ and

$$L(x) \equiv \frac{\partial^2}{\partial x^2} - x \frac{\partial}{\partial x} . \qquad (45)$$

Equation (44) is derived from equation (41) in a straight-forward manner using the definitions above and the fact that $g(0,p) = 1 + 0(E^2)$. Some further details will be given in the next subsection when we deal with the many-particle case.

Equation (44) seems to have no reasonably simple analytic solution, but it is a well-behaved linear differential equation

and is susceptible to numerical methods. (See Appendix A.)
We plot in Figure 5 the function $f_o(x) \exp(-x^2/2)$. For small
frequencies (a) the real part is gaussian and the imaginary
part is a gaussian which grows with increasing frequency. At
intermediate frequencies (b) the imaginary part peaks at a
momentum which corresponds roughly to the angular velocity of
the field. This represents a sort of "surf-riding" effect.
For high frequencies (c) we have $f_o \sim x/\omega(\tau_1\tau_2)^{\frac{1}{2}}$.

The resulting Cole-Cole plots for various values of
τ_2/τ_1 are shown in Figure 6. The negative susceptibility at
high frequencies is characteristic of a harmonically oscil-
lating particle which accelerates in phase with the field.
In addition, Figure 7 shows the absorption χ'' as a function of
frequency for various values of τ_2/τ_1.

2. Many Particles

The susceptibility in this case is given by

$$\frac{\chi}{N} = < e^{-i\theta_o} > = \int e^{-i(\varphi_o - \omega t)} P(\underline{\varphi}, \underline{p}, t) d^N\varphi d^N p$$

$$= (2\pi I T)^{N/2} \int d^N p f(\underline{p}) \exp(-\underline{p} \cdot \underline{p}/2IT) \qquad (45)$$

where we understand all quantities to be taken to linear order
in $E/2T$, which we then equate to unity. We shall write the
equation for f and show that

$$f = f_o(x_o) + 2(v/2T) f_1(x_o, x_1) + 0(v/2T)^2, \qquad (46)$$

where $x_i = p_i/IT$. We shall then consider the function f_1 and neglect the higher order terms.

The Fokker-Planck equation for this case is

$$\frac{\partial \rho}{\partial t} = \sum_i \left\{ E\sin(\varphi_i - \omega t) - v(\sin(\varphi_i - \varphi_{i-1}) + \sin(\varphi_i - \varphi_{i+1})) \right\} \frac{\partial \rho}{\partial p_i}$$

$$-\sum_i \frac{p_i}{I} \frac{\partial \rho}{\partial \varphi_i} + \eta \sum_i \frac{\partial}{\partial p_i} \left(p_i \rho + IT \frac{\partial \rho}{\partial p_i} \right) \qquad (47)$$

Define $\Phi = \rho \exp(\sum_k p_k^2/2IT)$. The viscous term now becomes

$$\eta \sum_i \frac{\partial}{\partial p_i} \left[\left(p_i \Phi - p_i \Phi + IT \frac{\partial \Phi}{\partial p_i} \right) \exp\left[-\sum_k p_k^2/2IT \right] \right]$$

$$= \eta \sum_i \left(IT \frac{\partial^2 \Phi}{\partial p_i^2} - p_i \frac{\partial \Phi}{\partial p_i} \right) \exp\left[-\sum_k p_k^2/2IT \right]$$

$$= \tau_2^{-1} \sum_i (L(x_i)\Phi) \exp\left(-\sum_k x_k^2/2 \right) \qquad (48)$$

As before, we set

$$\Phi = \sum_{\{n_j\}} \exp(i \sum_j n_j \theta_j) \Phi_{\{n_j\}}(\underline{p}) \qquad (49)$$

and keep those terms proportional to $\exp(i\theta_o)$. This gives

$$-i\omega f(\underline{p}) = \frac{iE}{2} \left(\frac{p_o}{IT} + \frac{p_{-1}}{IT} \Phi_{-1,1,0} + \frac{p_1}{IT} \Phi_{0,1,-1} \right)$$

$$+ \frac{v}{2i} \left\{ \left(\frac{p_o}{IT} - \frac{\partial}{\partial p_o} \right) \left(\Phi_{001} + \Phi_{100} - \Phi_{0,2,-1} - \Phi_{-1,2,0} \right) \right.$$

$$- \left(\frac{p_{-1}}{IT} - \frac{\partial}{\partial p_{-1}} \right) \left(\Phi_{100} - \Phi_{-1,2,0} \right) - \left(\frac{p_1}{IT} - \frac{\partial}{\partial p_1} \right) \left(\Phi_{001} - \Phi_{0,2,-1} \right)$$

$$- i \frac{p_o}{I} f(\underline{p}) + \tau_2^{-1} \sum_i L(x_i) f. \qquad (50)$$

Here the central subscript refers to the zero[th] sidechain, and

we have used the fact that $\phi_{\{n_j\}}$ differs from a pure gaussian by $O(E^2)$ if $\sum_j n_j = 0$. Rewriting the above in dimensionless variables and using translational invariance gives

$$\left[\sum_i L(x_1) + i\left(\omega\tau_2 - x_0\left(\frac{\tau_2}{\tau_1}\right)^{\frac{1}{2}}\right)\right]f(\underline{x})$$

$$= -i\left(\frac{\tau_2}{\tau_1}\right)^{\frac{1}{2}} \frac{E}{2T}(x_0 + x_{-1}\phi_{-110} + x_1\,\phi_{01-1})$$

$$+i\left(\frac{\tau_2}{\tau_1}\right)^{\frac{1}{2}} \frac{V}{2T}\left\{\left(x_0 - \frac{\partial}{\partial x_0}\right)\left(f(\underline{x}^+) + f(x^-) - \phi_{02-1} - \phi_{-120}\right)\right.$$

$$\left. -\left(x - 1 - \frac{\partial}{\partial x_{-1}}\right)\left(f(\underline{x}^-) - \phi_{-1,2,0}\right) - \left(x_1 - \frac{\partial}{\partial x_1}\right)\left(f(\underline{x}^+) - \phi_{0,2,-1}\right)\right\}$$

$$(51)$$

where, if $f(\underline{x}) = f(\ldots x_{-1}, x_0, x_1, \ldots)$

then $\qquad f(\underline{x}^+) = f(\ldots x_0, x_1, x_2, \ldots)$

and $\qquad f(\underline{x}^-) = f(\ldots x_{-2}, x_{-1}, x_0, \ldots)$. $\qquad (52)$

All the terms on the right hand side of (51) are linear in $E/2T$ (which we now set to unity) and it is now clear that we can write equation (46), where f_0 satisfies (44) and

$$\left[L(x_0) + L(x_1) + i\left(\omega\tau_2 - x_0\left(\frac{\tau_2}{\tau_1}\right)^{\frac{1}{2}}\right)\right]f_1(x_0, x_1)$$
$$= i\left(\frac{\tau_2}{\tau_1}\right)^{\frac{1}{2}}(x_1 + (x_0 - x_1)f_0(x_1) + \frac{\partial}{\partial x_1} f_0(x_1)). \qquad (53)$$

We have used a modified relaxation method to solve this equation. (See Appendix B.) The solution enables us to calculate the first order correction to the susceptibility, according to

$$\chi = \chi_o + 2\left(\frac{V}{2T}\right)\chi_1 + \theta\left(\frac{V}{2T}\right)^2$$

$$\chi_1 = \frac{1}{2\pi}\int dx_o \; e^{-x_o^2/2}\int dx_1 \; e^{-x_1^2/2} \; f_1(x_o,x_1) \; . \tag{54}$$

Typical results are shown in Figures 8, 9, and 10.

VI. Dynamic Correlation Functions

The susceptibility is related to a time-dependent correlation function according to [11]

$$(x_i x_k)_\omega = \frac{T}{\pi\omega}\ \chi_{ik}''(\omega) \tag{55}$$

or, for our case,

$$\frac{1}{\pi}\int_0^\infty < \cos\ \varphi_0(t)\ \cos\ \varphi_1(o) > e^{i\omega t}\ dt = \frac{1}{2\pi\omega}\left(\frac{v}{2T}\right)\chi_1''(\omega) \tag{56}$$

and

$$< \cos\ \varphi_0(t)\ \cos\ \varphi_1(o) > = \int_{-\infty}^\infty (2\pi\omega)^{-1}\left(\frac{v}{2T}\right)\chi_1''(\omega)e^{i\omega t}d\omega \tag{57}$$

where we neglect terms higher than linear in $(v/2T) \equiv x$.

For the viscous case we had

$$\chi = (1 + 2x - iz)^{-1} + 0(x^2)$$
$$= (1 - iz)^{-1} + 2x/(1-iz)^2 + 0(x^2) \tag{58}$$

so that

$$\chi_1^{(viscous)} = - (1 - iz)^{-2}$$
$$\chi_1''^{(viscous)} = -2z/(1 + z^2)^2 \tag{59}$$

Here we define $z \equiv \omega\tau_1 = \omega$ if we take $\tau_1 = 1$. We then have

$$< \cos\ \varphi_0(t)\cos\ \varphi_1(o) >^{(viscous)} = - \frac{v}{2T}\int_{-\infty}^\infty \frac{1}{2\pi}\ e^{izt}\ \frac{2dz}{(1+z^2)^2}$$

$$= - \tfrac{1}{2}\left(\frac{v}{2T}\right)\left(1 + t\right)e^{-t}. \tag{60}$$

We have numerically evaluated these correlation functions for three non-viscous cases, and these are shown in Figures 11 and 12. The errors on the curve $\tau_2 = 0.3$ are particularly large, so that this curve should not be taken too seriously.

One should observe, however, that (1) for large τ_2 the time scale of the correlations appears to vary like $\tau_2^{\frac{1}{3}}$, and (2) the correlation reaches a broad maximum before decaying. The first may be understood by noting that the characteristic angular velocity in the problem is $\frac{1}{I} < p^2 >^{\frac{1}{2}} = (\tau_1 \tau_2)^{-\frac{1}{2}}$. The second follows from noting that a measurement of $\cos \varphi_0(0)$ corresponds to a measurement of the force field on a neighboring particle at time zero, and this will be reflected in the position of the particle at some later time.

VII. Non-Einstein Damping

We have begun to examine the effect on the single-particle susceptibility of a random force more complex than the Einstein case we have used thus far. Such a force, which we describe by its moments μ_i, must satisfy the conditions that the Maxwell-Boltzmann distribution be both stationary and stable.

In the absence of applied field we may write

$$\rho(p,t) = (1 + g(p,t))\exp(-p^2/2IT) \tag{61}$$

and

$$\frac{\partial \rho}{\partial t} = \sum_{n=1}^{\infty} (-1)^n \frac{1}{n!} \frac{\partial^n}{\partial p^n} (\mu_n \rho). \tag{62}$$

The stationarity condition may be satisfied by choosing, for any n,

$$\mu_{2n} = (2n)! \, \xi_n IT$$
$$\mu_{2n-1} = -(2n-1)! \, \xi_n p . \tag{63}$$

This gives

$$\frac{\partial \rho}{\partial t} = \sum_{n=1}^{\infty} \frac{\partial^{2n-1}}{\partial p^{2n-1}} \left\{ \xi_n p \rho + \xi_n IT \frac{\partial \rho}{\partial p} \right\}$$

$$= \sum_{n=1}^{\infty} \frac{\partial^{2n-1}}{\partial p^{2n-1}} \left\{ \xi_n IT \frac{\partial g}{\partial p} \exp(-p^2/IT) \right\} \tag{64}$$

which clearly vanishes for g = constant. For a collection of N such pairs of moments (63), $g(x, t)$ will satisfy an equation of the form

$$\frac{\partial g}{\partial t} = \xi_N \frac{\partial^{2N} g}{\partial x^{2N}} - (2N-1)\xi_N x \frac{\partial^{2N-1} g}{\partial g^{2N-1}} + \ldots + h_2(x^2)\frac{\partial^2 g}{\partial x^2} + x h_1(x^2)\frac{\partial g}{\partial x} \tag{65}$$

where h_1 and h_2 are polynomials of degree $N - 1$. (The right hand side of (65) corresponds to the linear operator L of section V.) We may now consider the question of the stability of the Maxwell-Boltzmann distribution. For concreteness, we consider a distortion of the form $g \sim \cos \alpha x$. For α sufficiently small, such a distortion will decay in time as long as $h_2(x^2) > 0$. However, for large α the $(2N)$th derivative will be the dominant term, and, since the μ_n's are all positive-definite, this says that N must be odd to insure stability against a distortion which varies rapidly as a function of momentum.

We have done a few calculations using the method of Appendix A for the case $N = 3$, for which L takes the form

$$
\begin{aligned}
L(x) = {} & \xi_3\left(\frac{\partial^6}{\partial x^6} - 5x \frac{\partial^5}{\partial x^5}\right) + \left(\xi_2 + 10\xi_3(x^2 - 1)\right)\frac{\partial^4}{\partial x^4} \\
& + x(10\xi_3(3 - x^2) - 3\xi_2) \frac{\partial^3}{\partial x^3} \\
& + [1 + 5\xi_3(x^4 - 6x^2 + 3) + 3\xi_2(x^2 - 1)] \frac{\partial^2}{\partial x^2} \\
& + x[\xi_2(3 - x^2) - \xi_3(x^4 - 10x^2 + 15) - 1] \frac{\partial}{\partial x}
\end{aligned}
\tag{66}
$$

Some results are shown in Figure 13.

The susceptibility is determined by the function $f_0(x) = 1 + g(x)$, where g satisfies

$$
L(x)\, g(x) + i(\omega\tau_2 - (\tau_2/\tau_1)^{\frac{1}{2}})g(x) = -i\omega\tau_2.
\tag{67}
$$

One should note that the behavior of $g(x)$ for $|x| \rightarrow \infty$ is very different in the $N > 1$ case from the Einstein ($N = 1$) case. For $N = 1$, the dominant term on the left is $-i(\tau_2/\tau_1)^{\frac{1}{2}}xg(x)$, so that

$$g(x) \xrightarrow[|x| \rightarrow \infty]{} \omega(\tau_1\tau_2)^{\frac{1}{2}}/x \ . \tag{68}$$

For $N > 1$, the dominant term is $-\xi_N x^{2N-1} \frac{\partial}{\partial x} g(x)$, so that

$$g(x) \xrightarrow[|x| \rightarrow \infty]{} -i\omega\tau_2/(\xi_N x^{2N-2}) \ . \tag{69}$$

This results in decreased absorption at high frequencies.

VIII. Conclusions

We have produced a model polymer whose dielectric relaxation can be solved under a variety of conditions:

(1) At low frequencies,

$$\chi(\omega) \equiv \frac{2T}{N\mu^2} (\epsilon(\omega) - \epsilon_\infty) \xrightarrow[\omega \to 0]{} \frac{I_o(2x) - I_o'(2x)}{I_o(2x) + I_o'(2x)} \qquad (70)$$

where $x = v/2T$. For $x \gg 1$, $\chi(0) \to 1/8x$.

(2) In the viscous limit $\chi(\omega)$ may be expanded as a power series in x (high temperature expansion). The high frequency end of the Cole-Cole plot is shifted to the right by the interaction, but we find no indication of the slope's becoming finite near the origin. The shape of the curve depends only on the parameter $x = v/2T$.

(3) For the finite viscosity the problem is characterized by two times: a kinematic time $\tau_2 = \eta^{-1}$, and a relaxation time $\tau_1 = \eta I/T$, the viscous limit applying for $\tau_2 \ll \tau_1$. The non-interacting problem can be solved exactly (i.e., reduced to the solution of a differential equation), and a high temperature expansion exists in the more general case. In particular, dynamic correlation functions can be calculated for small x.

(4) Our method can be generalized to include a more complex random force. It is possible to construct a force for which the high frequency susceptibility moves to the

right of the Debye semicircle, even in the finite vis-
cosity non-interacting case.

None of the above cases convincingly reproduces a Cole-
Cole plot such as that of Figure 1, unless one is willing to
believe that the method of section VII, with a judicious choice
of moments (possibly an infinite number), can give such
behavior. A more likely cause of this effect is off-diagonal
viscosity, i.e., the random torque on a given sidechain
depends on the angular momentum of its neighbors. We have
neglected this possibility in deriving equation (21), but
it should be possible to generalize our methods to this case.

We believe this model to be interesting in its own right,
as well as shedding some light on the question of polymer
relaxation.

Acknowledgments

Appendix A. Method for Numerical Solution of (44)

This is a special case of a linear differential equation on the domain $-\infty < x < \infty$. The first step is to transform the real line into a finite interval by a change of variables such as

$$x = \alpha \tan \beta \phi . \qquad (A1)$$

Next we discretize the problem by dividing the interval $-\pi/2\beta < \phi < \pi/2\beta$ into N subintervals of length $\Delta = \pi/N\beta$, and replacing the derivatives by the corresponding symmetric finite differences, e.g.,

$$\frac{dy}{dx} \rightarrow \frac{y_{n+1} - y_{n-1}}{2\Delta} \qquad (A2)$$

$$\frac{d^2 y}{dx^2} \rightarrow \frac{y_{n+1} - 2y_n + y_{n-1}}{\Delta^2} \qquad (A3)$$

etc.

This procedure will give, for a differential equation of order $2m$, $(N + 1 - 2m)$ equations for $N + 1$ unknowns y_n. The remaining $2m$ equations are supplied by the boundary conditions. (The boundary conditions for (44) are $f_o = 1$ for $x = \pm \infty$.) It is known that under fairly general conditions the solution of the discrete problem will converge to that of the continuous problem as $N \rightarrow \infty$.

We have now reduced the problem to solving a set of complex linear equations

$$AY = B \tag{A4}$$

where A is an $(N + 1)$ by $(N + 1)$ matrix. In general, the computer time required to solve such a problem is at least $O(N^2)$, but by taking advantage of the fact that A is band-diagonal we may reduce the time to $O(N)$.

We have solved equation (44) using the SSP subroutine GELB[12], modified for complex numbers, and taking $\alpha = 3$, $\beta = \frac{1}{2}$, and $N = 40$. The time required to solve the equation for one set of parameters is less than one second on the Cornell University IBM 360/65.

Appendix B. Method of Solution of Equation (53)

This equation is of the form $L(x_1,x_2)f = R(x_1,x_2)$ where R is a known function and L is a linear operator. This may be converted into a discrete problem with $(N + 1)^2$ mesh points, but the matrix will not be band diagonal.

The usual relaxation method is as follows: We make an initial guess, satisfying the appropriate boundary conditions, for the solution f. The interior equations are of the form

$$L^D(x_i,x_j,f(x_i,x_j), \underline{x}^P, f(\underline{x}^P)) = R(x_i,x_j) \qquad (B1)$$

where $\underline{x}^P$ denotes the set of points immediately surrounding (x_i,x_j). A measure of the distance of our guess from the exact solution is

$$S = \sum_{i,j} S_{ij}$$

where

$$S_{ij} = L^D - R. \qquad (B2)$$

We then choose a point (x_i,x_j) and solve (B1) for $f(x_i,x_j)$. This sets S_{ij} to zero, but may increase the S_{kl}'s on the set $\underline{x}^P$, in which case the method may diverge.

The modification is to solve (B1) simultaneously on an n×n square of points (x_i,x_j). This reduces the number of points $\underline{x}^P$ relative to the number of points for which $S_{ij} = 0$, and should improve the chance of convergence.

We solved (53) using $N = 20$ and $n = 3$. The method always converged, while the usual relaxation method often diverged. However, convergence in some cases was rather slow.

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Figure Captions

Figure 1: Typical Cole-Cole plot of dielectric relaxation for a sidechain polymer. The dotted line is a semicircle.

Figure 2: Specific heat and correlation function $<-\exp i(\varphi_o - \varphi_1)>$ for a sidechain polymer. A discontinuity appears at $(v/2T) = 1.7$ for computational reasons.

Figure 3: Cole-Cole plots in the viscous limit for $x = 0$, 0.1, 0.2, 0.4, 0.6, 1.0. The crosses indicate the exact zero frequency results for $x = 0.6$ and $x = 1.0$. The dashed lines are lines of constant frequency.

Figure 4: Enlargement of the $x = 1.0$ plot of Figure 3. The dashed line is a semicircle.

Figure 5: The function $f_o(x) e^{-x^2/2}$ for $\tau_1 = \tau_2 = 1$ and (a) $\omega = .125$, (b) $\omega = 1.0$, and (c) $\omega = 4.0$.

Figure 6: Cole-Cole plots for $\tau_2/\tau_1 = 0.1$ (smallest curve), $\tau_2/\tau_1 = 0.316$, $\tau_2/\tau_1 = 1.0$, $\tau_2/\tau_1 = 3.16$, and $\tau_2/\tau_1 = 10.0$ (largest curve). The dashed line is a semicircle.

Figure 7: Absorption χ'' for the same five cases as in Figure 6. Curve A is $\tau_2/\tau_1 = 0.1$; curve E is $\tau_2/\tau_1 = 10$. The dashed line is $z/(1 + z^2)$.

Figure 8: The change in absorption $(-\chi_1'')$ for (A) $\tau_2/\tau_1 = 0$, (B) $\tau_2/\tau_1 = .316$, (C) $\tau_2/\tau_1 = 1.0$, (D) $\tau_2/\tau_1 = 3.16$.

Figure 9: χ_1' (solid line) and χ_1'' (dashed line) for $\tau_2/\tau_1 = 1.0$.

Figure 10: Cole-Cole plots for $\tau_2/\tau_1 = 1.0$ and $v = 0$ (upper
            curve) and $(v/2T) = 0.15$ (lower curve).

Figure 11: The correlation function χ_1''/ω for (A) $\tau_2/\tau_1 = 0$,
            (B) $\tau_2/\tau_1 = .316$, (C) $\tau_2/\tau_1 = 1.0$, (D) $\tau_2/\tau_1 = 3.16$.

Figure 12: The correlation function $< \cos \theta_0(t) \cos \theta_1(0) >$
            for the same cases as Figure 11.

Figure 13: Cole-Cole plots for non-Einstein damping: $\xi_2 = 2/3$,
            $\xi_3 = 1/15$, and $\tau_2/\tau_1 = 0.1$ (upper curve), $\tau_2/\tau_1 = 1.0$ (lower curve). The dashed line is a semicircle.

Figure 1

1.0 0.9 0.8 0.7 0.6 0.5 0.4 0.3 0.2 0.1 0

0 1 2 3 4 5
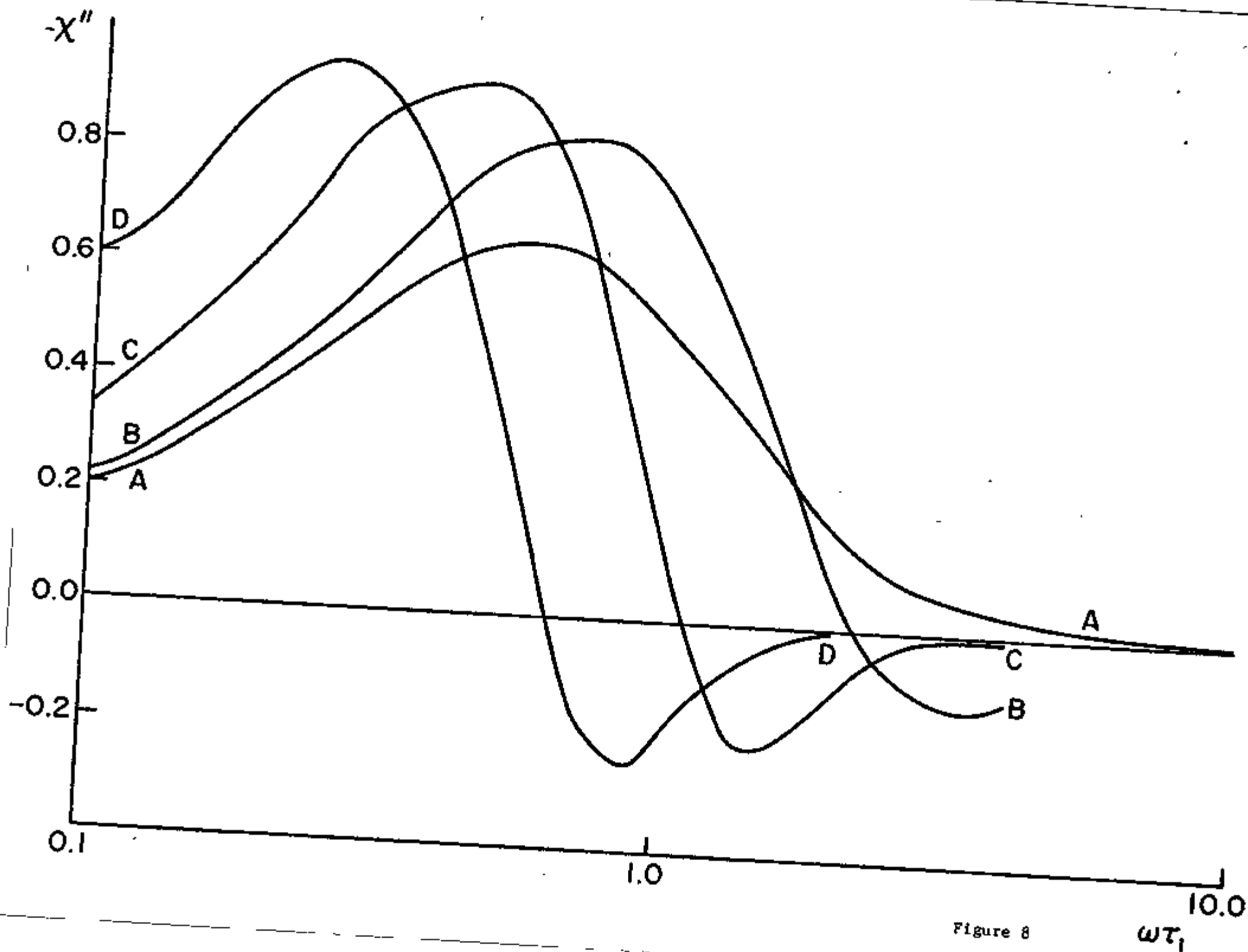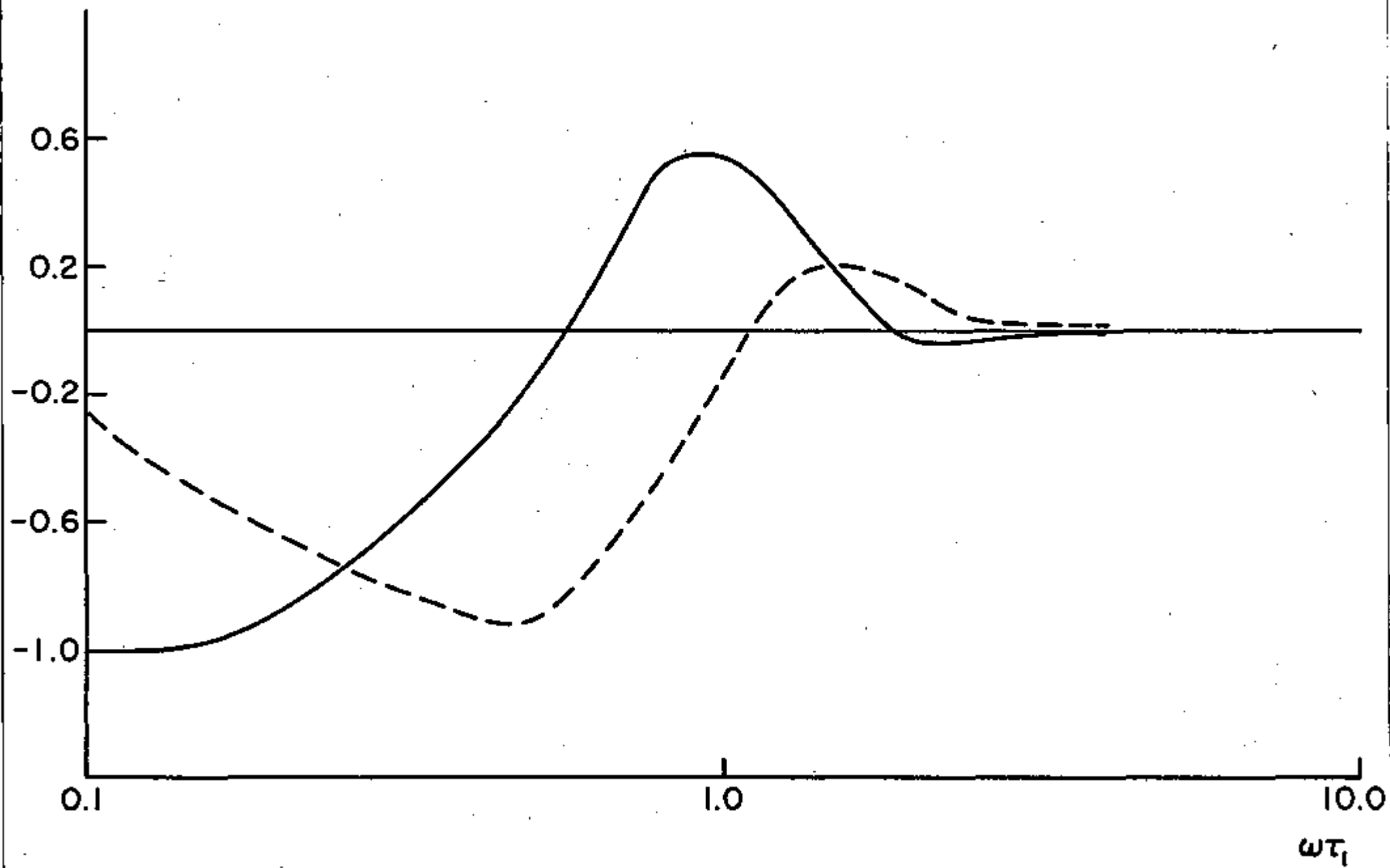
$\dfrac{v}{2T}$
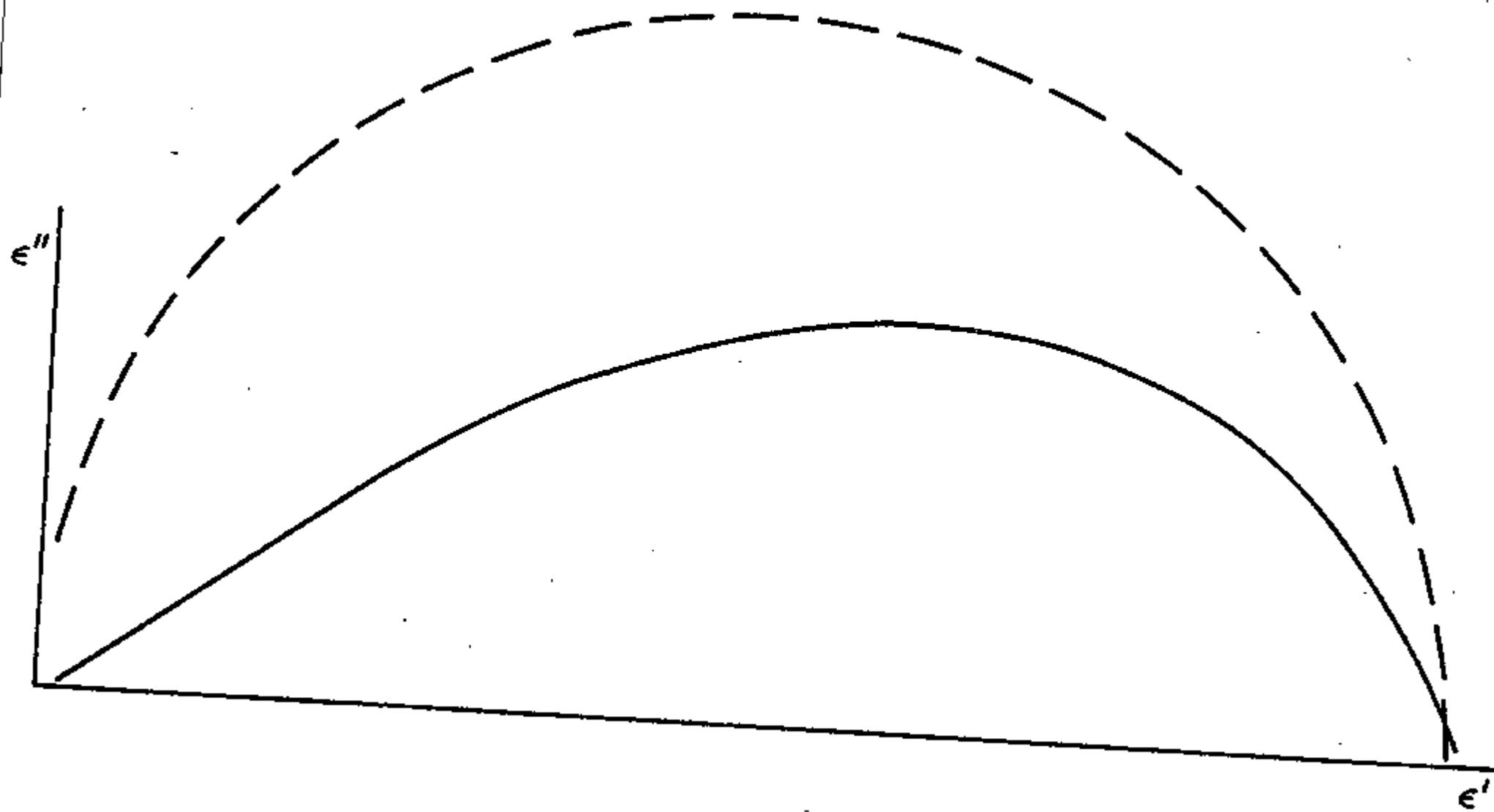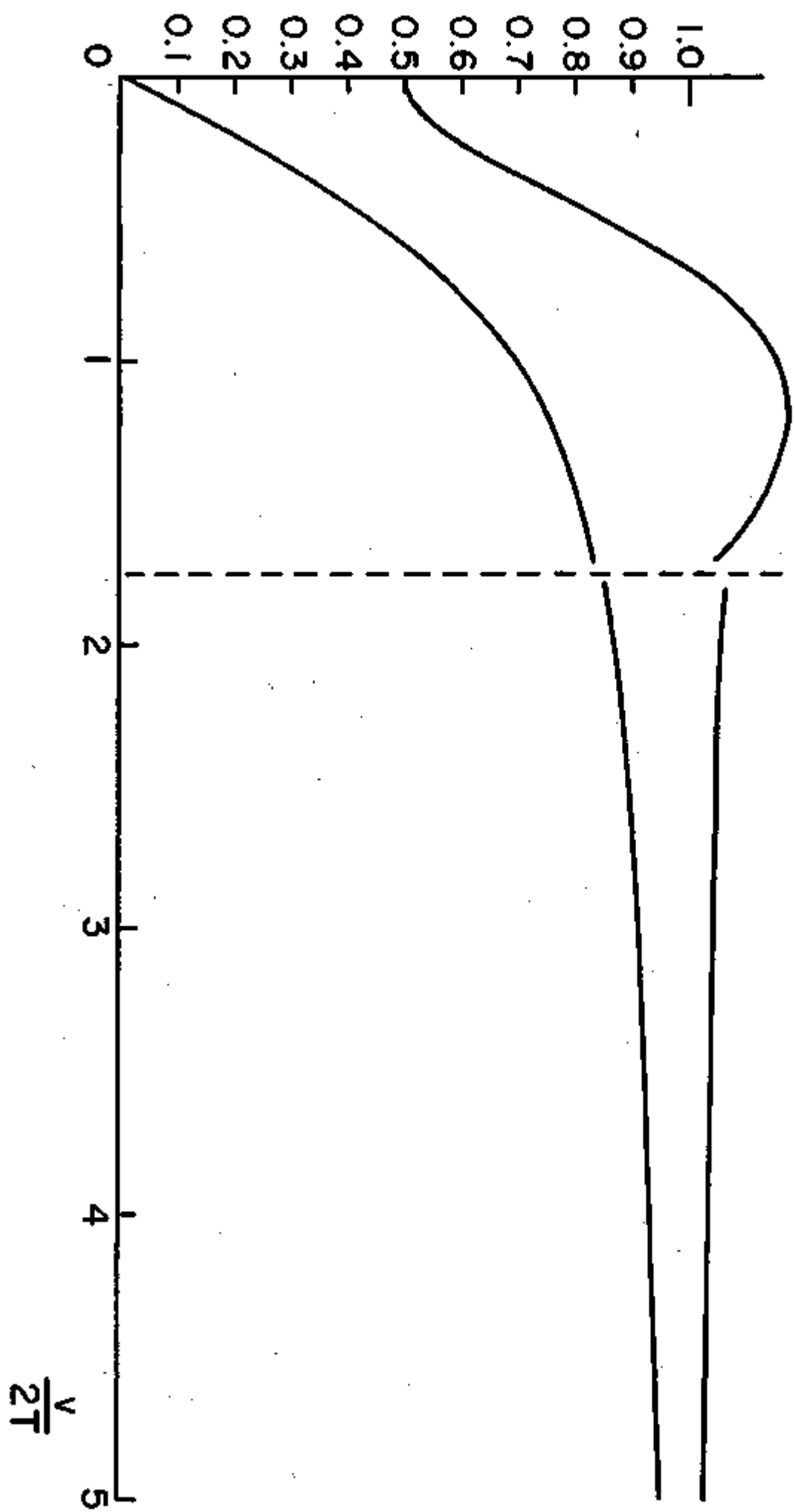
Figure 2

Figure 3

Figure 4

(a)

(b)

(c)
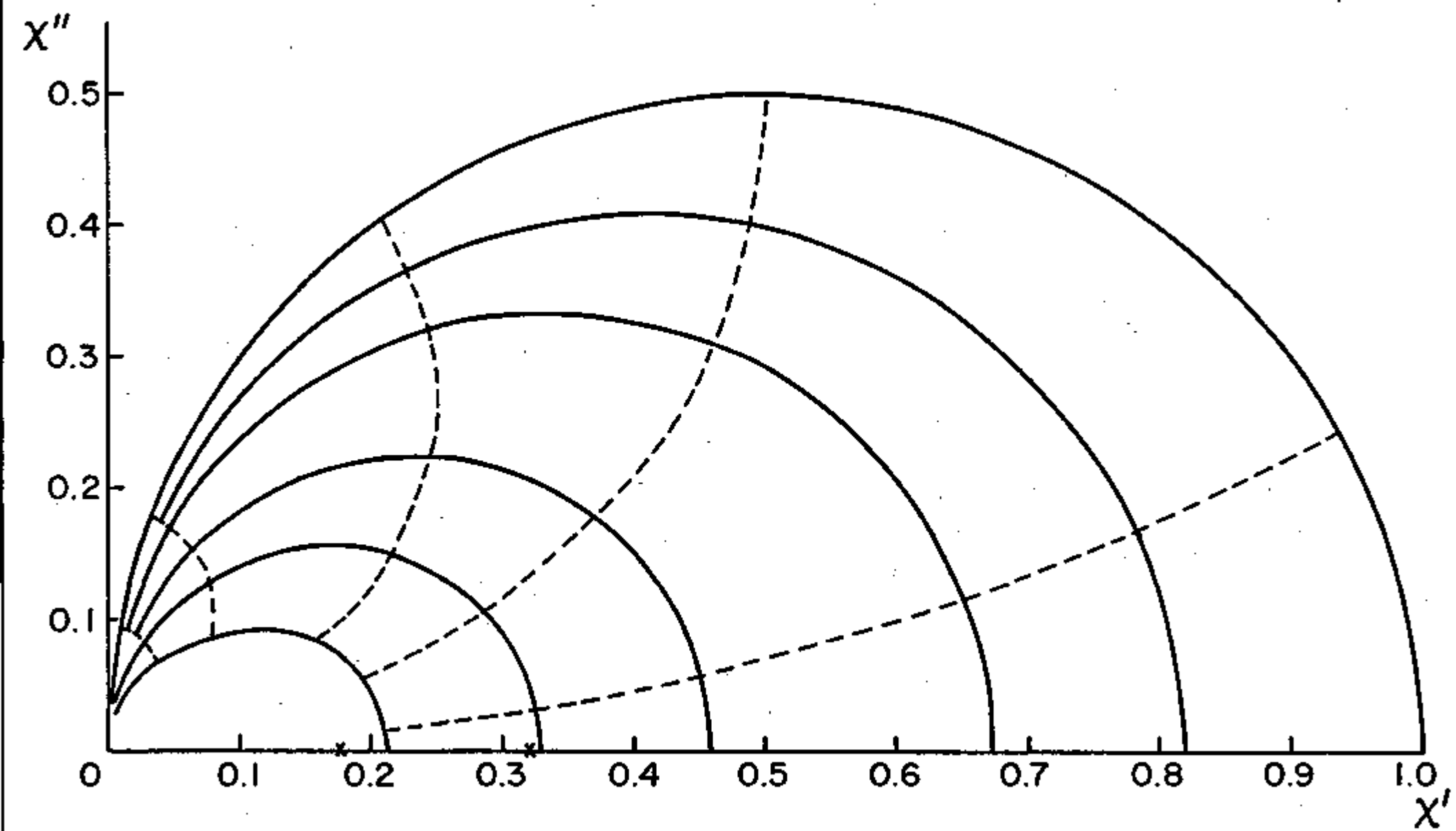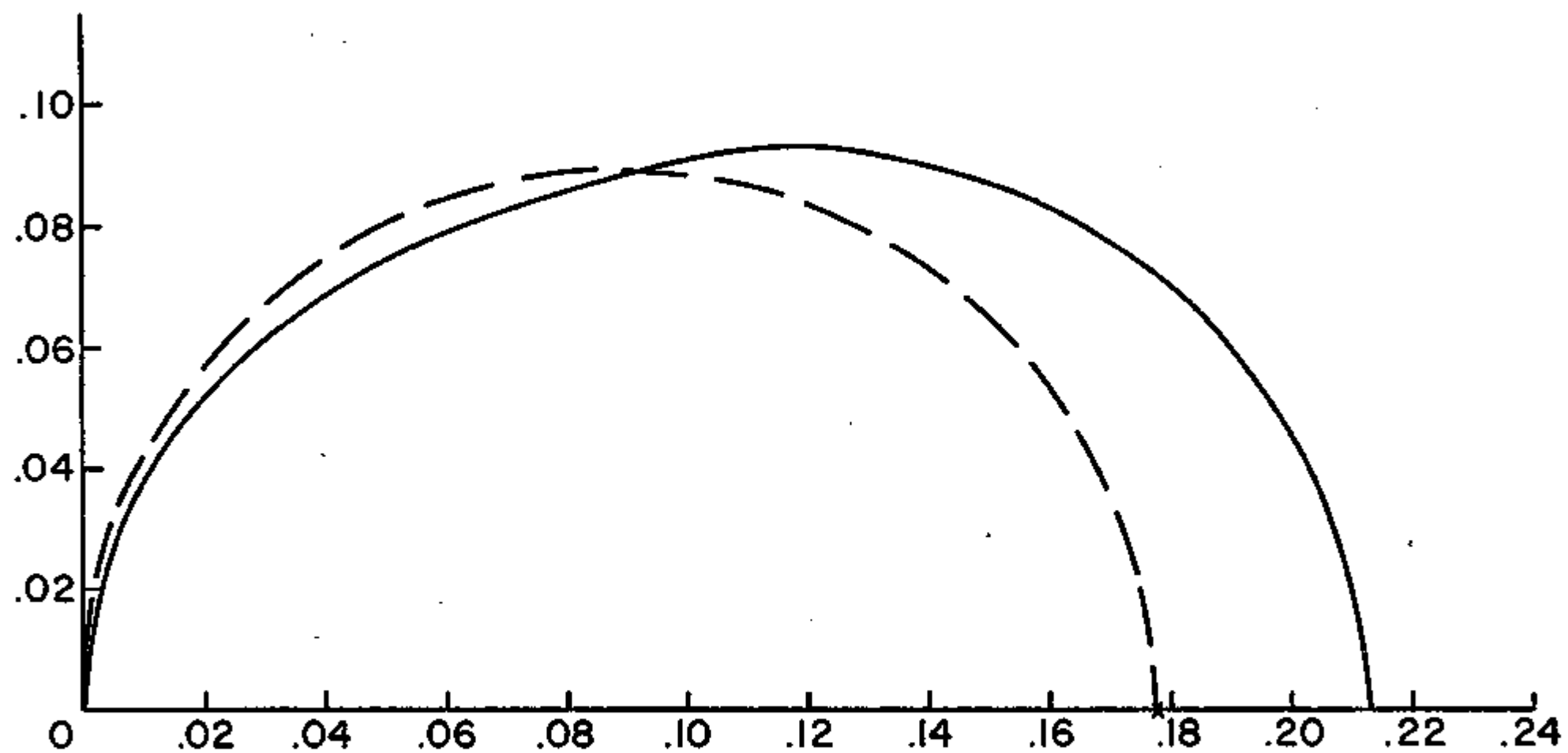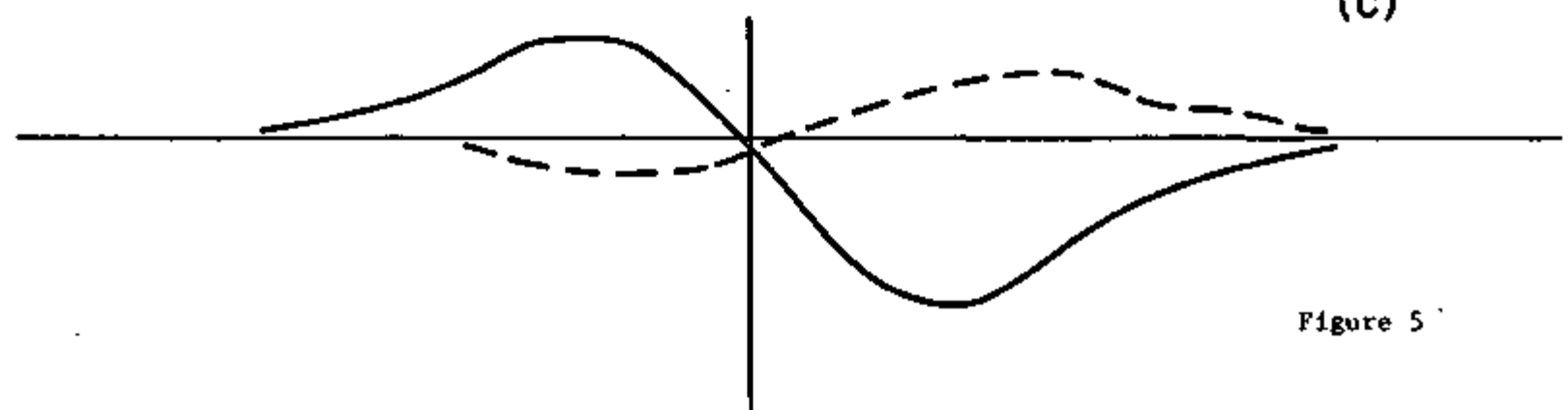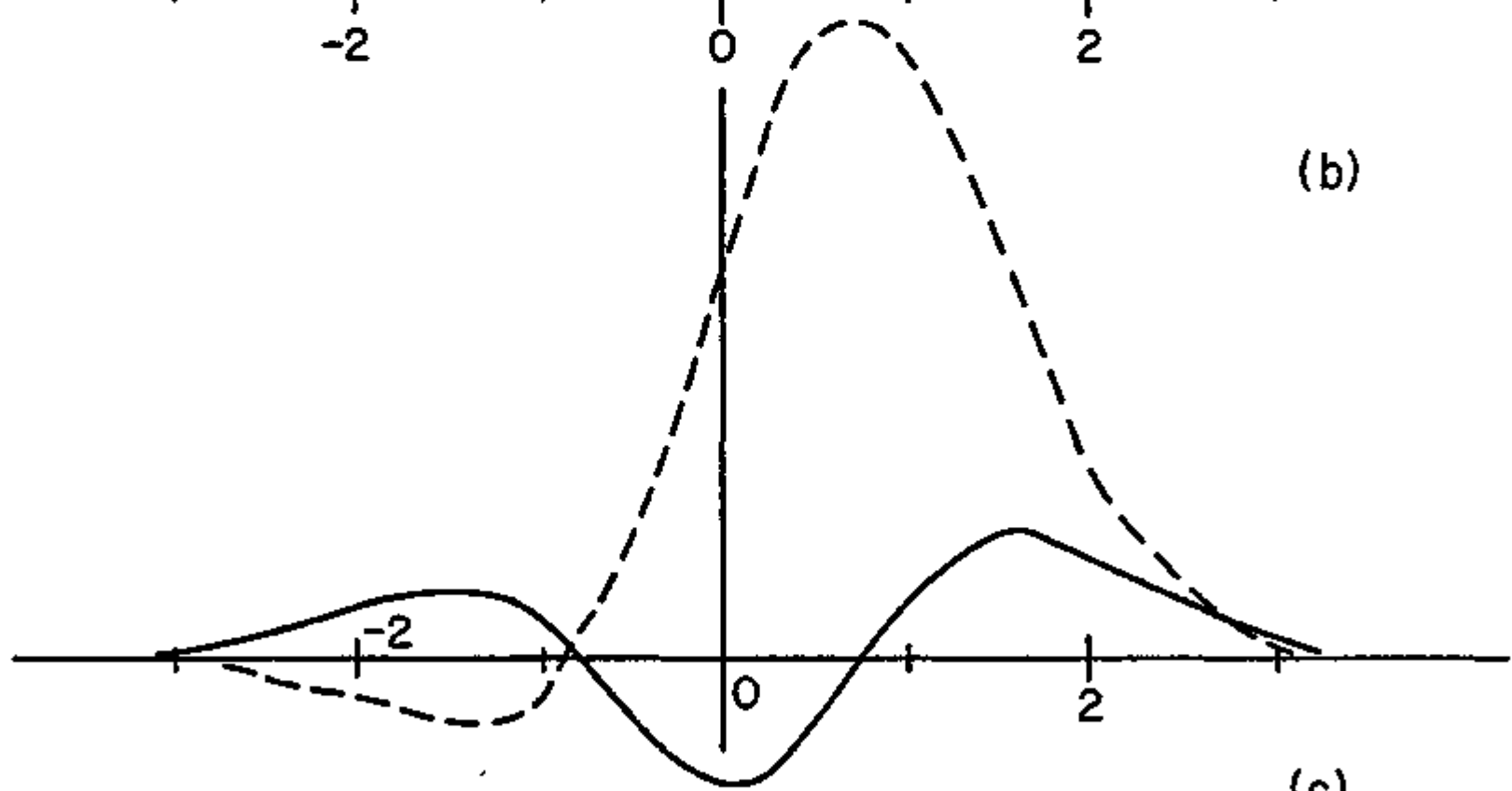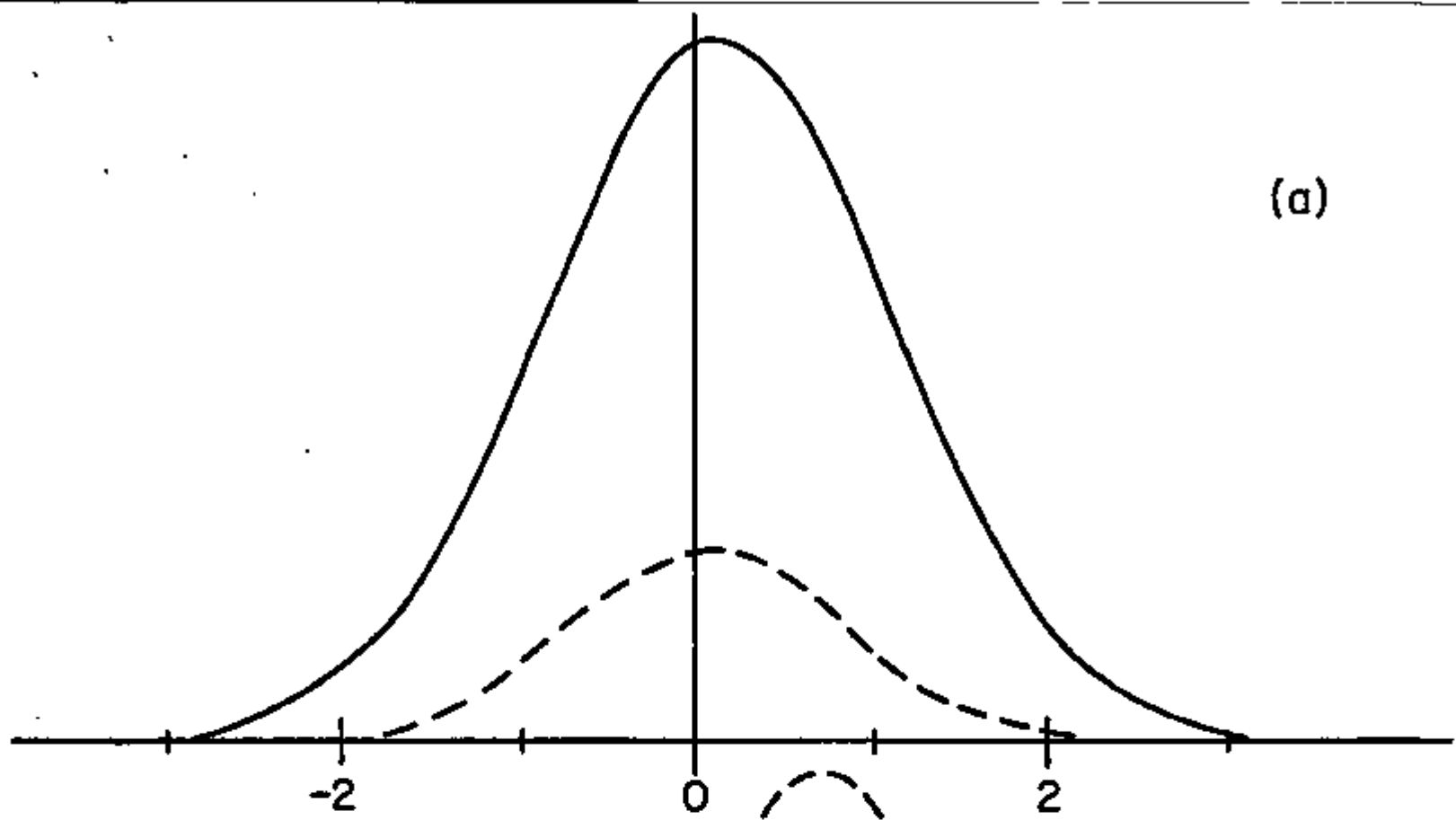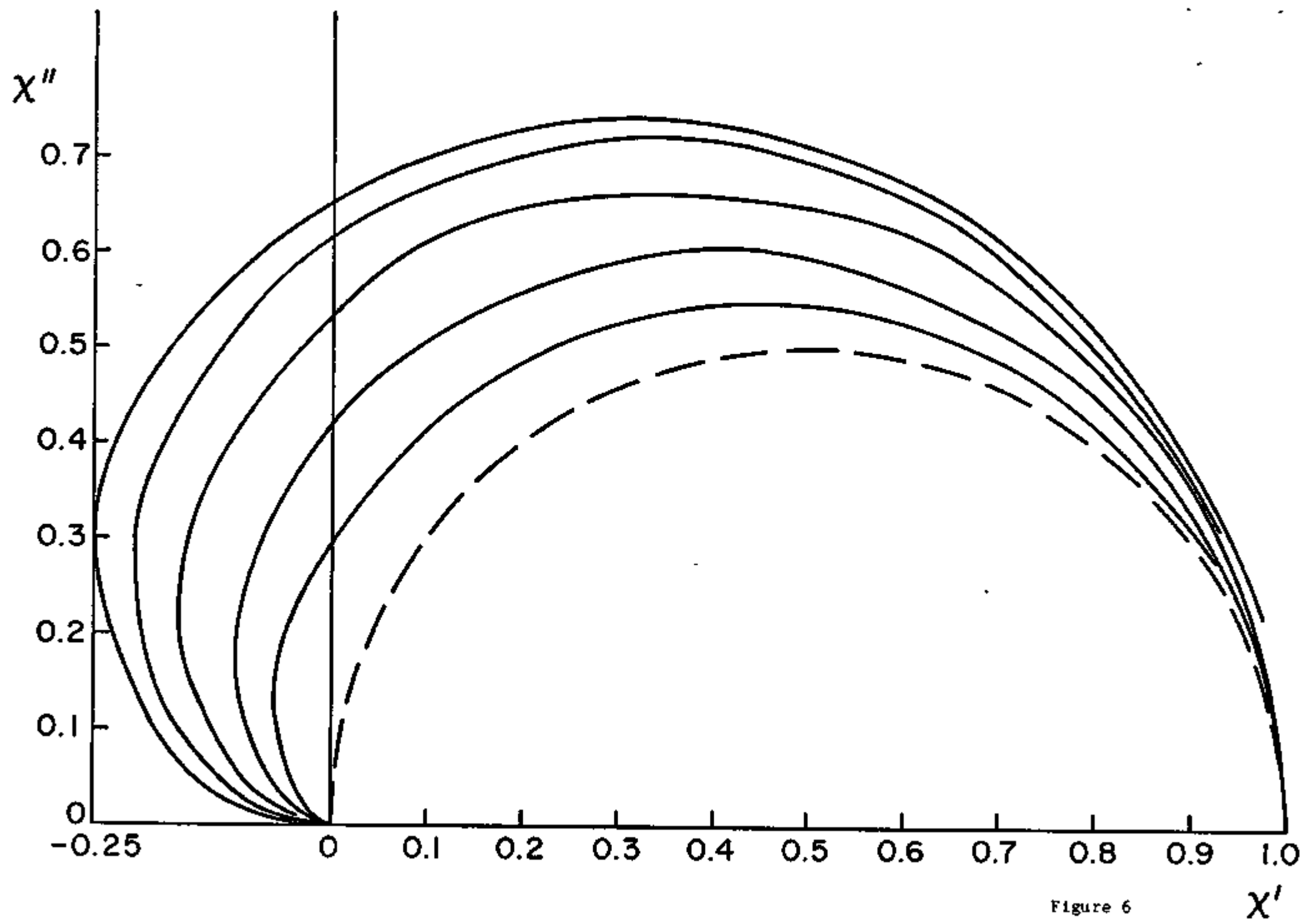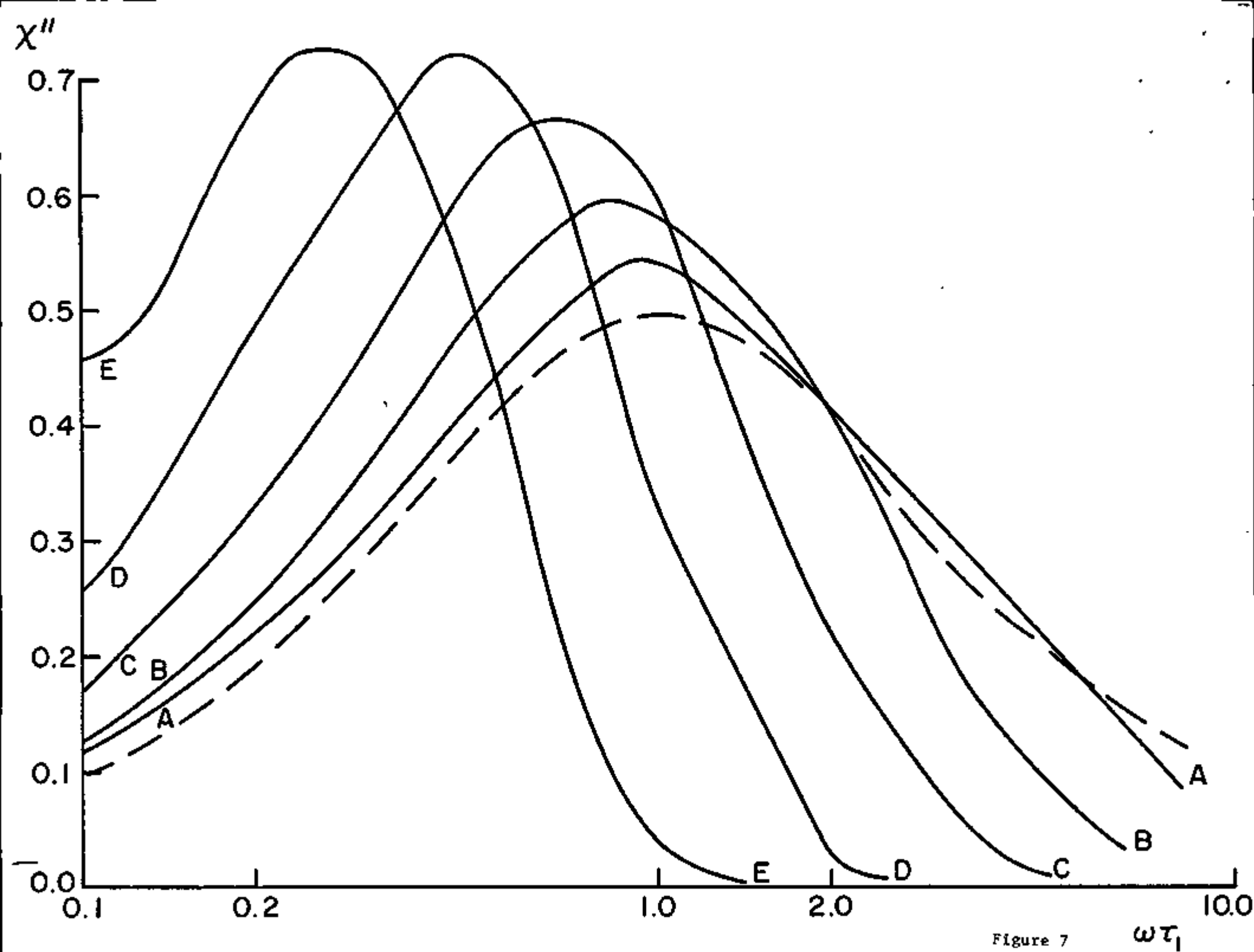
Figure 5

Figure 6

Figure 7
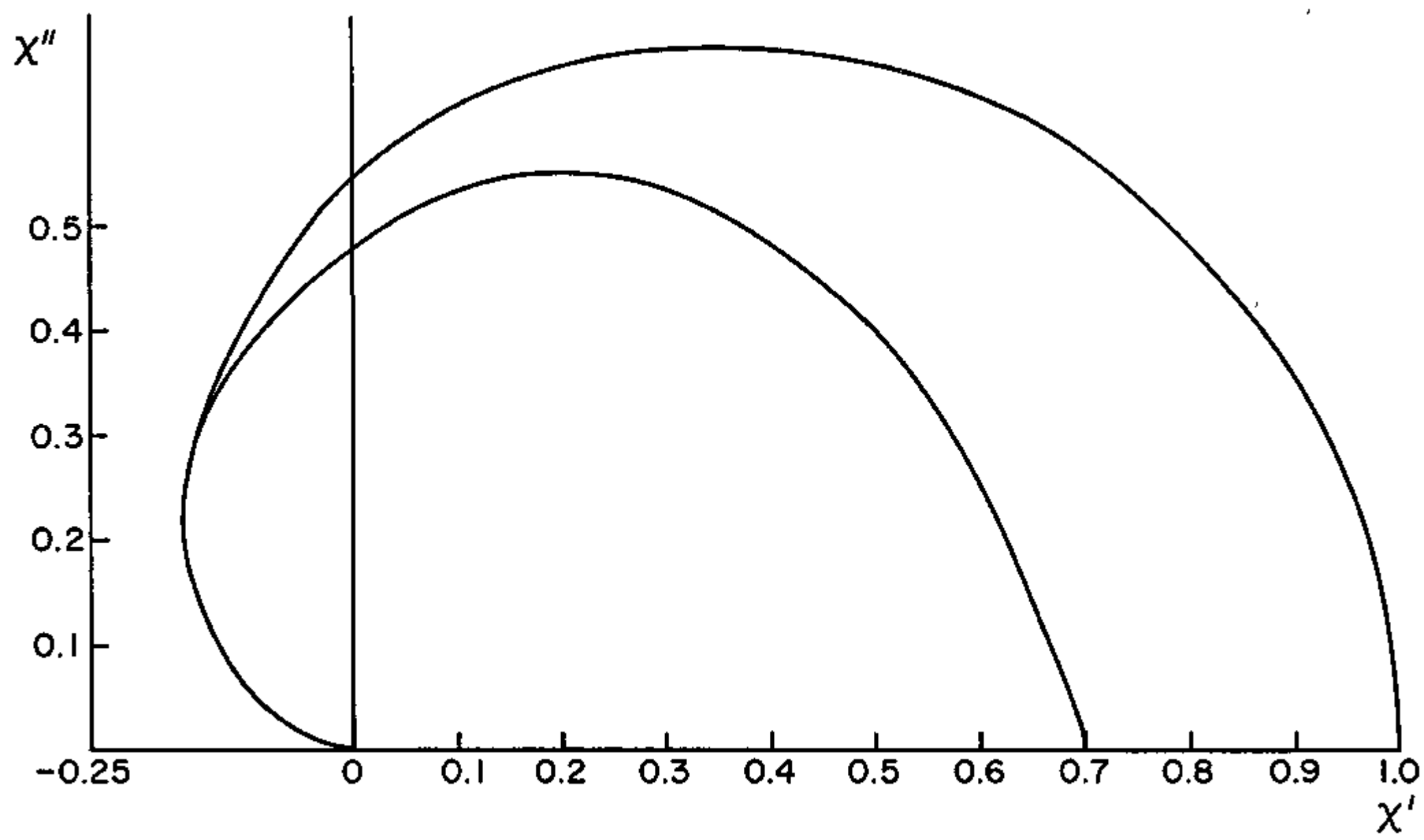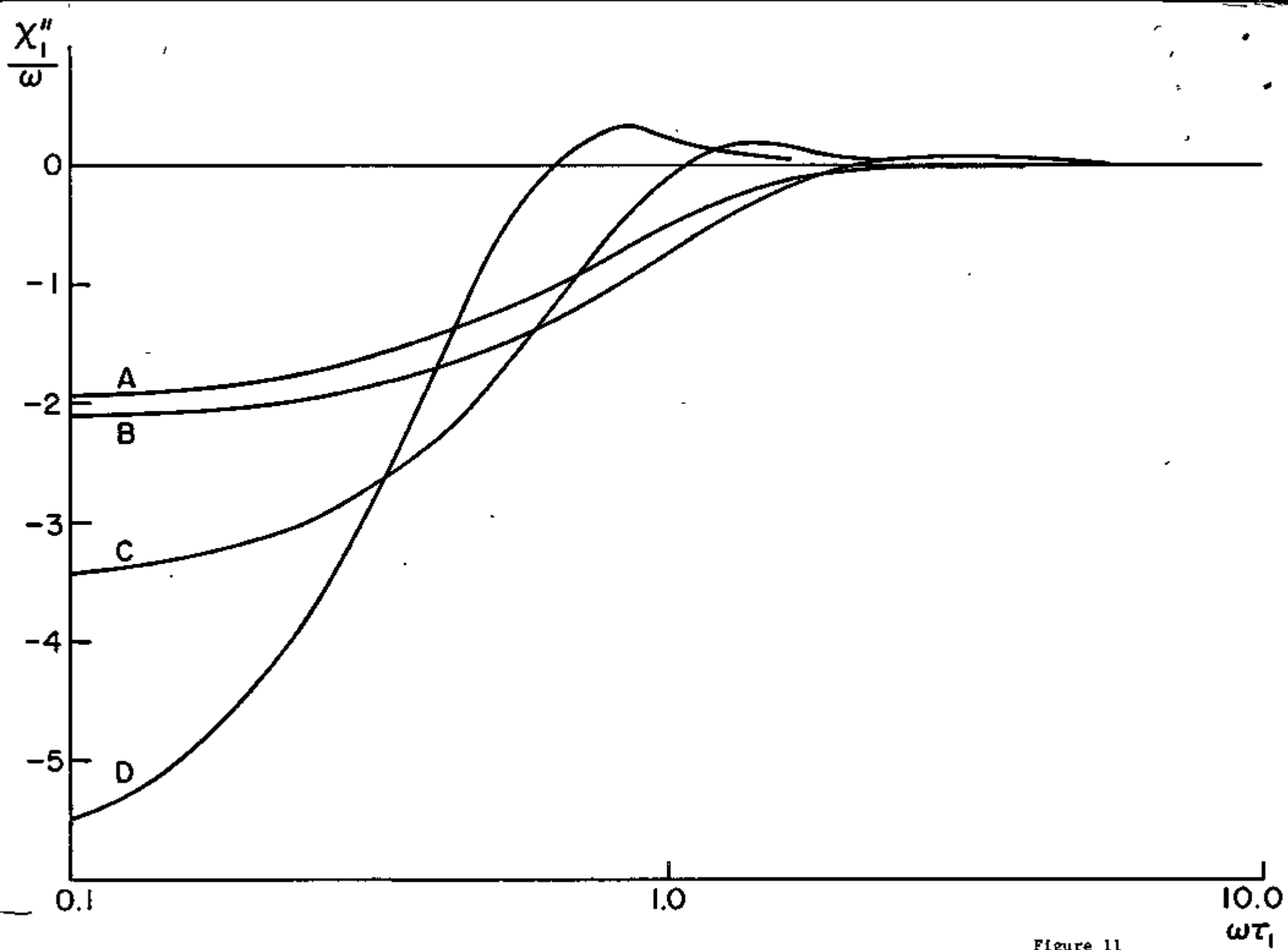
Figure 8

Figure 9

Figure 10

Figure 11

$\tau_2=0.3$

$\tau_2=3.16$

$\tau_2=1.0$

$(1+t)e^{-t}$

0   1.2   2.4   3.6   4.8   6.0   7.2   8.4   9.6 t

Figure 12

Figure 13