

低溫에서의 固體 重合體의 力學的 에너지 緩和에  
對한 線形反應 理論\*

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Linear Response Theory for the Mechanical Energy Relaxation  
of Solid High Polymers at Low Temperature\*

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요 약. 글라스(glass) 전이온도 이하에서 고체 중합체들의 역학적 분광학의 여러 현상들을 이론적으로 기술하는 데 적용될 線形 반응 이론을 제안하였다. 시료에 의한 에너지 분산을 어떤 시간 相關函數들로 나타내었다. Liouville 연산자를 Kirkwood의 확산식 연산자로 대체하면, 여기에서 얻은 결과로부터 다리결합을 한 중합체들의 에너지 상실과 완화에 대한 Kirkwood의 결과가 나옴을 보였다. 완화시간을 계산하는 방법을 보이기 위하여 상관함수들을 계산하는 근사법을 고찰하였다. 여기에서 제안한 이론과 저온에서 매달린 (pendant) 시클로헥실기들을 가진 고체 중합체들의 역학적 에너지 완화 현상을 기술하는 데 사용된 한 모형 이론과의 관련성을 찾아 보기 위해, 이 근사법을 써서 二重우물 퍼텐셜 모형을 고찰하였다.

**ABSTRACT.** Linear response theory is proposed to be applied for theoretical description of the phenomena in mechanical spectroscopy of solid high polymers below glass transition temperatures. The energy dissipation by sample is given in terms of certain time correlation functions. It is shown that the result leads to the result by Kirkwood on the energy loss and relaxation of cross-linked polymers, if the Liouville operator is replaced by the diffusion equation operator of Kirkwood. An approximation method of calculating the correlation functions is considered in order to show a way to calculate relaxation times. Using the approximation method, we consider a double-well potential model model for energy relaxation, in order to see a connection between the present theory and a model theory used in mechanical energy relaxation phenomena of solid polymers containing pendant cyclohexyl groups at low temperature.

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1. INTRODUCTION

Mechanical energy relaxation phenomena in solid high polymers below glass transition temperatures have been experimentally investigated by various experimental techniques<sup>1-3</sup>. The experimental data obtained, however, have not been subjected to extensive theoretical investigations, although there are a couple of typical systems studied in a model theory. Notably, an example is the model which regards the energy dissipation as achieved by a passage of particles (groups or molecules) over the potential barrier between two potential wells, which was the principal model used by Heijboer<sup>3</sup>. Such theory is hardly general. Therefore it seems desirable to have a general theory of mechanical energy relaxation phenomena in solid polymer systems at low temperature that does not necessarily have to be confined to a particular model for the description of molecular processes involved.

In mechanical relaxation experiments solid samples of polymer are subjected to strain or stress and subsequently the response of the system is recorded. Since the samples are viscoelastic, when they are subjected to oscillatory perturbation (strain or stress), there is usually a phase lag in the response as well as a decrease in the amplitude of oscillation. Since the two observables are intimately related to the energy relaxation phenomena of the system, a study of such phenomena could lead to rich information on the structure and its relationship to the mechanical properties of solid polymers.

Since the oscillatory perturbations used in experiments are in general small in magnitude compared with, say, the internal energy of the system of interest, linear response theory<sup>4-6</sup> appears well suited for the nonequilibrium statistical mechanical description of mechanical energy relaxations. In this article we propose to

use linear response theory for mechanical energy relaxation phenomena and show certain time correlation functions necessary for calculation of experimental observables. We also discuss the connection of the present approach to other existing theories. More specifically, we shall discuss the relationship between the present approach and the theory<sup>7</sup> of Kirkwood on mechanical energy loss in cross-linked polymers, which appears to be the first nonequilibrium statistical mechanical theory for such phenomena. We also consider the double-well potential model for mechanical energy relaxation phenomena as an example of another comparison.

Suppose that time-dependent stress  $\mathcal{C}(t)$  is applied on the sample. Then strain  $G(t)$  is generated by the system as a response. In the linear regime we have the following relationship<sup>1</sup> between them:

$$G(t) = \int_0^\infty d\tau A(\tau)\mathcal{C}(t-\tau), \quad (1-1)$$

where  $A(\tau)$  is the modulus. The Fourier-Laplace transform of  $A(\tau)$  is defined by

$$\hat{A}(\omega) = \int_0^\infty d\tau A(\tau)e^{i\omega\tau}, \quad (1-2)$$

which is a complex function of  $\omega$ . If the stress is oscillatory in time with frequency  $\omega$ , i. e.,

$$\mathcal{C}(t) = \mathcal{C}_0 \exp(i\omega t), \quad (1-3)$$

then the energy dissipation  $\langle E \rangle$  per unit volume of the sample may be shown<sup>1</sup> to be equal to

$$\langle E \rangle = \frac{1}{2} \omega \hat{A}''(\omega) |\mathcal{C}_0|^2, \quad (1-4)$$

where

$$\hat{A}''(\omega) = \text{Im} \hat{A}(\omega). \quad (1-5)$$

The  $\hat{A}''(\omega)$ , which is often called relaxation modulus, can be measured in terms of the phase lag  $\delta(\omega)$  defined by

$$\tan \delta(\omega) = \hat{A}''(\omega) / \hat{A}'(\omega), \quad (1-6)$$

where

$$\hat{A}'(\omega) = \text{Re} \hat{A}(\omega) \quad (1-7)$$

In the subsequent sections we will be concerned with a molecular theory to calculate  $\hat{A}''(\omega)$  and  $\hat{A}'(\omega)$  in terms of molecular interactions and other pertinent molecular parameters.

## 2. LINEAR RESPONSE THEORY AND MECHANICAL ENERGY RELAXATION

In order to apply linear response theory to the situation in hand, it is necessary to consider first the Hamiltonian. The Hamiltonian  $\mathcal{H}_0$  for the system at equilibrium may be written as follows:

$$\mathcal{H}_0 = T(p_1, \dots, p_N) + V_0(q_1, \dots, q_N), \quad (2-1)$$

where  $T$  and  $V_0$  are the kinetic and potential energy, respectively. This Hamiltonian is time-independent. When time-dependent external force is applied on the system, the energy of the system is no longer conserved and the Hamiltonian becomes time-dependent. In the present case we may write as

$$\mathcal{H} = \mathcal{H}_0 - F(q_1, \dots, q_N) \mathcal{J}(t) \quad (2-2)$$

Here the stress may be also a function of space coordinates, but we will assume that it is a function of time only (It is not difficult to remove this assumption). This means that the stress is uniformly constant over the sample. Thus  $\mathcal{J}(t)$  is assumed to have the form as given by (1-3) with  $\mathcal{J}_0$  as a constant.  $F(q_1, \dots, q_N)$  is a certain function of coordinates characteristic of the system of interest. This function is often not known, but it is sufficient for our purpose here to assume that it exists. Later, we shall discuss a couple of examples for  $F$  (see Sec. 3).

Then, according to the fluctuation-dissipation theorem<sup>5,6,8</sup>, the energy dissipation  $\langle E \rangle$  may be given as

$$\langle E \rangle = \frac{\omega}{2\hbar} \tanh\left(\frac{1}{2}\beta\hbar\omega\right) \langle \frac{1}{2}[F(0), F(t)]_+ \rangle_{\rho_0} \mathcal{J}_0^2, \quad (2-3)$$

where

$$F(t) = \exp(i\hbar^{-1}t\mathcal{H}_0) F(q) \exp(-i\hbar^{-1}t\mathcal{H}_0), \quad (2-4)$$

$$\langle [F(0), F(t)]_+ \rangle_{\rho_0} \equiv \int_{-\infty}^{\infty} dt e^{i\omega t} T_2 \{ \rho_0 [F(0)F(t) + F(t)F(0)] \}, \quad (2-5)$$

and

$$\rho_0 = \exp(-\beta\mathcal{H}_0) / T_2 \exp(-\beta\mathcal{H}_0) \quad (2-6)$$

the canonical ensemble density matrix. Here we have used the quantum mechanical formalism. We thus see that the energy dissipation is directly related to the Fourier transform of the time correlation function of  $F(q_1, \dots, q_N)$ ,

$$C(t) = \langle \frac{1}{2}[F(0)F(t) + F(t)F(0)] \rangle \equiv \langle \frac{1}{2}[F(0), F(t)]_+ \rangle, \quad (2-7)$$

where  $\langle \dots \rangle$  means the equilibrium ensemble average.

By comparing (2-3) with the phenomenological equation for  $\langle E \rangle$ , (1-4), we obtain the molecular expression for  $\hat{A}''(\omega)$ ;

$$\hat{A}''(\omega) = \hbar^{-1} \tanh\left(\frac{1}{2}\beta\hbar\omega\right) \hat{C}(\omega), \quad (2-8)$$

where

$$\hat{C}(\omega) = \int_{-\infty}^{\infty} dt e^{i\omega t} C(t). \quad (2-9)$$

Eq. (2-8) is the desired formula that can serve as the starting equation for the theory of mechanical energy relaxation phenomena. Since in experiments the frequency dependence of  $\langle E \rangle$  in essence is measured at various temperature, Eq. (2-8), when calculated as a function of  $\omega$ , would supply the energy absorption profile. In this sense the situation with the mechanical energy relaxation phenomena is quite parallel

to the conventional electromagnetic spectroscopy and by calculating (2-8) and (2-3), we are in effect calculating the line shapes in mechanical spectroscopy. We believe that this analogy would be useful in developing further the present theory, as it would enable us to benefit in such effort from the fairly well developed theories of line shape in the electromagnetic spectroscopy.

If we ignore non-commutativity of the operators  $F(0)$  and  $F(t)$ ,  $C(t)$  may be written as

$$C(t) = \langle F(0)F(t) \rangle. \quad (2-10)$$

Furthermore, the frequency usually is so small that the condition

$$\hbar\omega/kT \ll 1 \quad (2-11)$$

is satisfied in general. If we use (2-10) and (2-11) in (2-8), we then obtain

$$\begin{aligned} \hat{A}''(\omega) &= -\frac{\omega}{2kT} \hat{C}(\omega) \\ &= -\frac{\omega}{2kT} \langle F(0)F(t) \rangle_{\omega}. \end{aligned} \quad (2-12)$$

We will be concerned with this form of  $\hat{A}''(\omega)$  in the following discussions. Given a specific form for  $F(q)$ , one can in principle calculate the time correlation function. However, such calculation is not practicable without approximations due to the difficulty associated with the many-body nature of the problem. Approximate calculations of  $C(t)$  will be more fully dealt with in future communications.

In the next section we shall consider a connection of the present theory with the theory<sup>7</sup> of Kirkwood in a related subject, since it would reveal the general nature of linear response theory as applied to the mechanical energy relaxation phenomena and also would render a further support for the present approach to the phenomena.

### 3. A CONNECTION WITH KIRKWOOD'S THEORY

In 1946 Kirkwood<sup>7</sup> proposed a theory on mechanical energy relaxation of cross-linked polymers, based on a Brownian motion model, which appears to be the first nonequilibrium statistical mechanical theory for the phenomena. Nevertheless, it seems that the theory has not been pursued further except by Bueche<sup>9</sup> who considered a similar idea in a somewhat different formalism in the subsequent years.

Kirkwood proposed to use a diffusion equation for the distribution function in his theory and proceeded to solve the equation in a perturbation theory. He expanded the distribution function in a series of the applied stress  $\omega_0$  and obtained the first order correction to the equilibrium distribution function, since the process linear in  $\omega_0$  was of interest. With the distribution function thus obtained, he calculated  $\hat{A}(\omega)$  (in our notation). Here we would like to see how (2-12), for example, is related to his result. This should not be regarded as an idle exercise, because it would show the unifying feature of (2-12) as well as a way to calculate  $C(t)$  with a model theory like Kirkwood's.

In order to facilitate this discussion, we observe that (2-4) may be written in the following form:

$$F(t) = \exp(iLt)F(q) \quad (3-1)$$

where the Liouville operator  $L$  is defined by

$$LF = \hbar^{-1}[\mathcal{H}_0, F] = \hbar^{-1}(\mathcal{H}_0F - F\mathcal{H}_0). \quad (3-2)$$

We also note that in the classical mechanical formalism it is only necessary to replace  $L$  with the corresponding classical Liouville operator  $L^{(c)}$  defined by

$$L^{(c)} = -i \sum_{j=1}^N \left[ \frac{\partial \mathcal{H}_0}{\partial p_j} \frac{\partial}{\partial q_j} - \frac{\partial \mathcal{H}_0}{\partial q_j} \frac{\partial}{\partial p_j} \right].$$

(3-2) i. e.,

Kubo<sup>10</sup> showed that it is possible to replace the Liouville equation with a corresponding stochastic Liouville equation for the description of the evolution of the system. This means that we may replace the Liouville operator  $L$  in (3-1) with the operator corresponding to the diffusion equation used by Kirkwood. For this we assume that it is permissible to replace  $L$  with  $L^{(c)}$ , i. e., the classical description is acceptable.

Kirkwood assumed that the chain segments go through rotary diffusion in the space of angles  $q_i$ ,  $i=1, \dots, N$ , defined by the adjacent planes containing two sets of adjacent chain segments. This assumption can be stated mathematically in a diffusion equation for the distribution function in the  $q$ -space.

Then in this  $q$ -space the time correlation function  $C(t)$  may be written in the form,

$$C(t) = \int dq_1 \cdots dq_N F(q_1, \dots, q_N) t^{\otimes} [F(q_1, \dots, q_N) \rho_0], \quad (3-3)$$

where the diffusion operator is defined by

$$\begin{aligned} \mathcal{D}\psi &\equiv \nabla \cdot \mathbf{D} \cdot [\nabla\psi + \psi \nabla V_0/kT] \\ &= \nabla \cdot \mathbf{D} \cdot [\nabla\psi - \psi \nabla \ln \rho_0] \end{aligned} \quad (3-4)$$

The gradient operator  $\nabla$  is defined in the  $q$ -space of  $N$  dimension. Here  $\rho_0$  is now defined by

$$\mathcal{D}\rho_0 = 0, \quad (3-5)$$

that is, the equilibrium ensemble distribution function. It is important to note that the potential function appearing in (3-4) is  $V_0$ , not  $V_0 + \mathcal{H}_1(t)$ . This can be understood if we recall that we are considering the response of the system to the perturbation  $\mathcal{H}_1(t)$  to a linear approximation in linear response theory.

It is convenient to define a Hermitean operator  $\mathcal{L}$  by the relation<sup>11</sup>,

$$\mathcal{D}(\psi \rho_0) = -\rho_0 \mathcal{L}\psi \quad (3-6)$$

$$\mathcal{L}\psi = -[\nabla \cdot \mathbf{D} \cdot \nabla\psi + \nabla \ln \rho_0 \cdot \mathbf{D} \cdot \nabla\psi] \quad (3-7)$$

It is interesting to note that this  $\mathcal{L}$  is precisely the negative of  $L$  defined by Kirkwood (see Eq. (13) of Ref. 7). Then  $C(t)$  can be written in the form,

$$C(t) = \int dq_1 \cdots dq_N \rho_0 F(q_1, \dots, q_N) e^{-t\mathcal{L}} F(q_1, \dots, q_N) \equiv \langle F | e^{-t\mathcal{L}} | F \rangle. \quad (3-8)$$

Now we define an eigenvalue problem for  $\mathcal{L}$ ;

$$\mathcal{L}\varphi_\lambda = \lambda\varphi_\lambda, \quad (3-9)$$

where  $\varphi_\lambda$  is the eigenfunction of  $\mathcal{L}$  with the eigenvalue  $\lambda$ . With normalized eigenfunctions  $\{\varphi_\lambda\}$ , which are also orthogonal to each other

$$\begin{aligned} \delta_{\lambda\lambda'} &= \langle \varphi_{\lambda'} | \varphi_\lambda \rangle \\ &= \int dq_1 \cdots dq_N \rho_0 \varphi_{\lambda'}^* \varphi_\lambda, \end{aligned} \quad (3-10)$$

we obtain the correlation function in the form,

$$C(t) = \sum_\lambda e^{-\lambda t} \langle F | \varphi_\lambda \rangle \langle \varphi_\lambda | F \rangle, \quad (3-11)$$

and by taking the Fourier transform, we obtain  $\hat{C}(\omega)$  in the form,

$$\hat{C}(\omega) = \sum_\lambda \frac{2\tau_\lambda |\langle F | \varphi_\lambda \rangle|^2}{1 + (\tau_\lambda \omega)^2}, \quad (3-12)$$

where

$$\tau_\lambda = 1/\lambda. \quad (3-13)$$

Now in order to show the equivalence of (3-12) to the Kirkwood formula, we first consider  $\langle F | \varphi_\lambda \rangle$ . It is given in the form,

$$\langle F | \varphi_\lambda \rangle = \int dq_1 \cdots dq_N \rho_0 F(q_1, \dots, q_N) \varphi_\lambda, \quad (3-14)$$

where we now must take for the space-dependent part of the perturbation<sup>7</sup>

$$F = \mathbf{R} \cdot \mathbf{e}_l = \sum_{i=1}^N r_i \cdot \mathbf{e}_i, \quad (3-15)$$

$r_i$  being the bond vector of the  $l$ th chain

segment and  $e_1$  the unit vector along the direction of stress applied. It is to be noted that in Kirkwood's theory  $r_i$  are functions of angles  $q_i$  between two planes containing two sets of sectors  $(r_i, r_{i-1})$  and  $(r_i, r_{i+1})$ , respectively. By taking the linear transformation

$$\phi_\lambda = \rho_0^{-1/2} \psi_\lambda \quad (3-16)$$

and

$$L_0 \equiv \rho_0^{1/2} \mathcal{L} \rho_0^{-1/2},$$

one can show that

$$L_0 = \nabla \cdot \mathbf{D} \cdot \nabla + u(q) \quad (3-17)$$

$$u(q) = \frac{1}{2kT} \nabla \cdot \mathbf{D} \cdot \nabla V_0 - \frac{1}{(2kT)^2} \nabla V_0 \cdot \mathbf{D} \cdot \nabla V_0 \quad (3-18)$$

That is,  $\phi_\lambda$  are the eigenfunctions of the eigenvalue problem considered by Kirkwood,

$$L_0 \phi_\lambda = \lambda \phi_\lambda.$$

This is Eq. (14) of Ref. 7. Therefore we may now write

$$\begin{aligned} \langle F | \phi_\lambda \rangle &= \int dq_1 \cdots dq_N (\mathbf{R} \cdot \mathbf{e}_1) \phi_\lambda \rho_0^{1/2} \\ &= A_0^{1/2} \int dq_1 \cdots dq_N (\mathbf{R} \cdot \mathbf{e}_1) \psi_\lambda e^{-V_0/2kT}, \end{aligned} \quad (3-19)$$

where

$$A_0^{-1} = \int dq_1 \cdots dq_N e^{-V_0/kT} \quad (3-20)$$

Since  $\phi_\lambda$  are exactly the same eigenfunctions as defined by Kirkwood, we have now shown that  $\langle F | \phi_\lambda \rangle$  is exactly the same as  $Z_\lambda$  defined by Kirkwood (Eq. (15) of Ref. 7). Therefore, we now see that Kirkwood's theory results from the linear response theory result, e. g., (2-10), if the Liouville operator is replaced by the corresponding diffusion operator. A moment of reflection would reveal that this should not be surprising because both linear response theory

and Kirkwood's theory are exploring the linear regime of energy relaxation phenomena and thus rely on a first order perturbation theory for the distribution function. This comparison also renders a support to our linear response theory approach to mechanical energy relaxation phenomena. Since the diffusion operator used here is only a model for the Liouville operator, the above comparison also implies that the linear response theory is inclusive of Kirkwood's theory and therefore may be regarded as more general.

#### 4. APPROXIMATE CALCULATION OF THE CORRELATION FUNCTION

If it is allowed to replace the Liouville operator with the corresponding diffusion operator, then (3-12) is exact with the exact eigenfunctions within the validity of linear response theory. However, it requires the eigenfunctions and the eigenspectrum, which are not necessarily simple to obtain except for some special cases. Therefore it is common to resort to suitable approximation methods to calculate  $\hat{C}(\omega)$ .

There are various techniques developed for calculating correlation functions. Since it is not our aim here to either develop another method or review all of them available, we shall simply indicate how far we can go with a known method, since such an effort would again indicate that mechanical spectroscopy could benefit much by making contacts with various theories in other disciplines of spectroscopy. Besides, the present section will serve as a preparation for the calculation made for a double-well potential model in the next section.

Here we shall use the well known projection operator technique<sup>11,12</sup>.

In order to use the projection operator formalism for (3-7) with  $F$  defined by (3-15), we introduce a set of dynamical variables  $\{A_i; i =$

1, ..., N} such that

$$A_i = r_i \cdot e_1 - \langle r_i \cdot e_1 \rangle. \quad (4-1)$$

Then obviously

$$\langle A_i \rangle = 0.$$

With thus defined  $A_i$  it is now possible to show

$$C(t) = \sum_{i,k} \langle A_i(0) A_k(t) \rangle \quad (4-2)$$

since

$$\langle F(0) \rangle = \langle F(t) \rangle = 0. \quad (4-3)$$

If (4-3) is not fulfilled, it is only necessary to add  $\langle F(0) \rangle \langle F(t) \rangle$  to the rhs of (4-2). Then the matrix of correlation functions  $A_{ik}$ , which are defined by

$$\begin{aligned} A_{ik}(t) &= \langle A_i(0) A_k(t) \rangle \\ &= \langle A_i(0) e^{-\mathcal{L}t} A_k(0) \rangle, \end{aligned} \quad (4-4)$$

where  $\mathcal{L}$  is defined by (3-6), satisfies a non-Markoffian evolution equation. This evolution is in the form<sup>11,12</sup>,

$$\frac{\partial}{\partial t} \underline{\mathcal{A}}(t) = -\underline{\mathcal{Q}} \cdot \underline{\mathcal{A}}(t) + \int_0^t d\tau K(t-\tau) \cdot \underline{\mathcal{A}}(\tau), \quad (4-5)$$

where

$$\underline{\mathcal{Q}}_{jm} = \sum_n \langle A_j \mathcal{L} A_m \rangle \Gamma_{mn}, \quad (4-6)$$

$$(\Gamma^{-1})_{jk} = \langle A_j A_k \rangle, \quad (4-7)$$

and with the projection operator  $\mathcal{P}$  defined by

$$\mathcal{P}_B = \sum_{jk} A_j \Gamma_{jk} \langle A_k B \rangle, \quad (4-8)$$

$$\begin{aligned} K_{jn}^{(B)} &= \sum_m \langle A_j \mathcal{L} (1 - \mathcal{P}) e^{-\mathcal{L}(1-\mathcal{P})t} \\ &\quad (1 - \mathcal{P}) \mathcal{L} A_m \rangle \Gamma_{mn}. \end{aligned} \quad (4-9)$$

The second term in (4-5) is the memory term. If the memory term can be neglected, the equation then takes the approximate form,

$$\frac{\partial}{\partial t} \underline{\mathcal{A}}(t) = -\underline{\mathcal{Q}} \cdot \underline{\mathcal{A}}(t). \quad (4-10)$$

The solution of (4-10) requires the solution of an N-dimensional eigenvalue problem: Let  $\underline{A}$  be a diagonal matrix such that

$$\underline{U}^{-1} \underline{\mathcal{Q}} \underline{U} = \underline{A} \quad (4-11)$$

and

$$\underline{\mathcal{A}}(t) = \underline{U} \underline{a}(t) \quad (4-12)$$

Then the solution  $\underline{a}(t)$  is easily obtained from (4-10) and we have for the correlation function  $A_{ik}$

$$A_{ik}(t) = \sum_j U_{ij} \exp(-\lambda_j t) A_{jk}(0). \quad (4-13)$$

Finally, the relaxation modulus to this approximation is given in the form,

$$\hat{A}''(\omega) = \frac{\omega}{kT} \sum_{j,k,l} \frac{U_{lj} \tau_j A_{jk}(0)}{1 + (\tau_j \omega)^2}, \quad (4-14)$$

where

$$\tau_j = 1/\lambda_j. \quad (4-15)$$

An explicit calculation of (4-14) requires knowledge of  $\underline{\mathcal{Q}}$ , which is rather complicated, for example, in Kirkwood's model. Since the formalism presented is sufficiently flexible as to be adopted to other suitable models, we shall introduce a further simplification for calculation of (4-14) in order to see if we can recover some known results.

We assume instead of (3-14) for  $F$  the following form resembling the Hookean model,<sup>9</sup>

$$F = \sum_i \alpha (q_i - q_i^0), \quad (4-16)$$

where  $\alpha$  is a constant and  $q_i$  this time denote the particle (bead) coordinates of polymer chain and  $q_i^0$  their equilibrium values. Then in this  $q$ -space we can still assume the diffusion equation (3-4).

The dynamical variables  $A_i$  now can be identified with

$$A_i = \alpha (q_i - q_i^0), \text{ etc.} \quad (4-17)$$

We further assume that the equilibrium cor-

relation of  $A_i$  are diagonal:

$$A_{jk}(0) = \langle A_j^2 \rangle \delta_{jk}. \quad (4-18)$$

This means that

$$(\underline{F}^{-1})_{jk} = \langle A_j^2 \rangle \delta_{jk}. \quad (4-19)$$

Then we obtain from (4-6)

$$\Omega_{jn} = \langle A_j \underline{L} A_n \rangle \langle A_n^2 \rangle. \quad (4-20)$$

Since we have

$$\begin{aligned} \langle A_j \underline{L} A_n \rangle &= \langle \nabla A_j \cdot \underline{D} \cdot \nabla A_n \rangle \\ &= \sum_{k,l} \langle \nabla_k A_j D_{kl} \nabla_l A_n \rangle \end{aligned} \quad (4-21)$$

and furthermore

$$\begin{aligned} \nabla_k A_j &= \alpha \nabla_k (q_j - q_j^0) \\ &= \alpha \delta_{kj}, \end{aligned} \quad (4-22)$$

the matrix elements  $\Omega_{jn}$  takes the form

$$\Omega_{jn} = \alpha^2 \langle D_{jn} \rangle \langle A_j^2 \rangle \quad (4-23)$$

Here the diffusion tensor represents interaction between particles. If we assume that the diffusion tensor is diagonal we obtain

$$\Omega_{jn} = \alpha^2 \langle D_j \rangle \langle A_j^2 \rangle \delta_{jn} \equiv \alpha^2 D_j^0 \langle A_j^2 \rangle \delta_{jn} \quad (4-24)$$

and then the relaxation time simply becomes

$$\tau_j^{-1} = \alpha^2 D_j^0 \langle A_j^2 \rangle. \quad (4-25)$$

If the particles are subjected to harmonic oscillation around the equilibrium positions, then we have

$$\langle A_j^2 \rangle = \frac{kT}{m_j \omega_j^2} \quad (4-26)$$

where  $m_j$  and  $\omega_j$  are respectively the mass and the frequency of the oscillation, and the relaxation time now takes the form,

$$\tau_j^{-1} = \alpha^2 D_j^0 kT / m_j \omega_j^2 \quad (4-27)$$

This result for the relaxation time is quite reminiscent of the result by Bueche<sup>9</sup>.

In this case the relaxation modulus  $\hat{A}''(\omega)$

becomes

$$\hat{A}''(\omega) = \frac{\omega}{kT} \sum_j \frac{\tau_j \langle A_j^2 \rangle}{1 + (\omega \tau_j)^2}, \quad (4-28)$$

where  $\langle A_j^2 \rangle$  and  $\tau_j$  are respectively given by (4-26) and (4-27).

Calculation of the correlation function  $C(t)$  are in progress with another approximation method and will be reported elsewhere.<sup>13</sup>

## 5. A DOUBLE-WELL POTENTIAL MODEL

The mechanical energy relaxation of pendant-cyclohexyl-group-containing polymers has been attributed<sup>3</sup> to tunnelling through and passing over a potential barrier by the pendant cyclohexyl group. In this model the relaxation is achieved essentially by one-dimensional motion along the "reaction coordinate" corresponding to the boat-boat conformational transition through and over a potential barrier. In order to accommodate this model in the present formalism, let us now confine the discussion to a one-dimensional version of the results in Sec. 4. In this model the "reaction mode" moves in the field of a one-dimensional effective potential which arises due to the interaction of the mode with the surrounding medium. Therefore, we have only one dynamical variable  $A_1$  which can be chosen as

$$A^0 = F(q)_1, \quad (5-1)$$

where  $q$  is the reaction coordinate. Since we can use the formalism presented in Sec. 4 for this study, we only give the result. The relaxation time may be calculated from (4-15). It is given by

$$\tau^{-1} = D \left\langle \frac{\partial F}{\partial q} \frac{\partial F}{\partial q} \right\rangle / \langle F^2 \rangle, \quad (5-2)$$

where  $F(q)$  is a function of  $q$  and  $D$  a diffusion constant instead of a tensor. In order to keep in line with Heijboer's model<sup>3</sup>, we shall assume



that the potential  $V_0$  is made of two potential wells separated by a potential barrier (see Fig. 1).

The cyclohexyl group (mode) moves in the one-dimensional potential well and has a probability to tunnel through the barrier to the other potential well which corresponds to the other conformation. Therefore the tunnelling and passage over the barrier are equivalent to a conformational flipping of the cyclohexyl group. The interaction of the cyclohexyl group with the surrounding is achieved in two ways: One is through the effective potential  $V_0$  and the other through the dissipation of energy which is accomplished phenomenologically through the frictional motion (The frictional motion is implied by the presence of the diffusion constant  $D$  in the formula).

In order to carry out the calculation of the relaxation time as a function of temperature, we expand  $V_0$  around  $q_A$  and  $q_B$  as follows:

$$\begin{aligned} V_0 &\approx V_A + F_A(q - q_A)^2, & -\infty < q < q_C \\ V_0 &\approx V_B + F_B(q - q_B)^2, & q_C < q < \infty. \end{aligned} \quad (5-3)$$

We wish to remark here that the calculations performed below are approximate and mathematical rigor is sacrificed for the sake of the

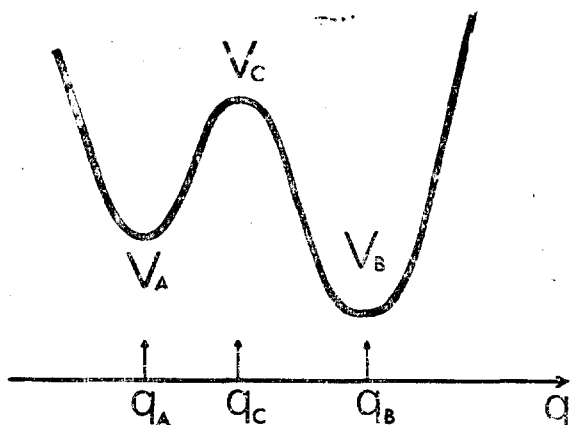


Fig. 1. A double well potential.

intuitive picture we wish to gain. The same attitude applies to (5-3) above. More rigorous calculations can be done, however, which would not give simple analytic forms for the results. We may write the correlation functions in the forms,

$$\left\langle \left( \frac{\partial F}{\partial q} \right)^2 \right\rangle = A_0 \int_{-\infty}^{\infty} dq e^{-\beta V_0} \left( \frac{\partial F}{\partial q} \right)^2, \quad (5-4)$$

and

$$\langle F^2 \rangle = A_0 \int_{-\infty}^{\infty} dq e^{-\beta V_0} F^2(q). \quad (5-5)$$

Here we assume that  $F(q)$  is a linear function of  $q$ , i. e.,

$$F(q) = \begin{cases} F_A(q - q_A), & q \leq q_C \\ F_B(q - q_B), & q \geq q_C. \end{cases} \quad (5-6)$$

If the range of the integrals (5-4) and (5-5) is divided into two regions,  $[-\infty, q_C]$  and  $[q_C, \infty]$ , and if the approximate forms of the potential are used in each interval as given in (5-3), then we can evaluate the integrals analytically. Without going into the details of calculation, we give the results as follows:

$$\begin{aligned} \left\langle \left( \frac{\partial F}{\partial q} \right)^2 \right\rangle &\approx (\pi kT)^{1/2} F_A^{3/2} \\ &\quad [e^{-\beta V_A} - \frac{1}{2}(F_A/\pi kT)^{1/2} \\ &\quad (q_C - q_A)^{-1} e^{-\beta V_C} + \dots] \\ &\quad + (\pi kT)^{1/2} F_B^{3/2} [e^{-\beta V_B} \\ &\quad - \frac{1}{2}(F_B/\pi kT)^{1/2} (q_B - q_C)^{-1} \\ &\quad e^{-\beta V_C} + \dots] \end{aligned} \quad (5-7)$$

and

$$\begin{aligned} \langle F^2 \rangle &\approx \frac{1}{2} kT F_A [(\pi kT/F_A)^{1/2} e^{-\beta V_B} \\ &\quad - (q_C - q_A) e^{-\beta V_C} + \dots] \\ &\quad + \frac{1}{2} kT F_B [(\pi kT/F_B)^{1/2} e^{-\beta V_A} \\ &\quad - (q_B - q_C) e^{-\beta V_C} + \dots], \end{aligned} \quad (5-8)$$

where  $V_C$  is the potential energy at  $q = q_C$ , the barrier maximum. In the case of the cyclohexyl group it is reasonable to assume that  $F_A \approx F_B$ . Then we obtain an approximate relaxation time

in the form,

$$\tau^{-1} \approx \gamma + \sigma e^{-Q/kT} \quad (5-9)$$

where

$$Q = V_C - V_A,$$

the potential barrier height referred to the well depth at  $A$ , and

$$\gamma = Dm\omega_f^2/kT, \quad \omega_f = (2F_A/m)^{1/2}, \quad (5-10)$$

$$\sigma = 2\pi D(m\omega_f^2/2\pi kT)^{3/2} \Delta q; \quad \Delta q = q_B - q_A. \quad (5-11)$$

Therefore as either  $Q \rightarrow \infty$  or  $T \rightarrow 0$ , the relaxation time tends to the value  $\tau^{-1}$ ,

$$\tau^{-1} \rightarrow \tau_\infty^{-1} = \gamma. \quad (5-12)$$

This means that even if the potential barrier is so high that there is little probability of passing over the barrier, the relaxation of mechanical energy is still possible due to the fact that the oscillator in the well  $V_A$  suffers a damping in motion due to its motion in the viscous medium with the diffusion constant  $D$ . The ratio  $\sigma/\gamma$  is

$$\begin{aligned} \sigma/\gamma &= (2/\pi)\omega_f \Delta q / \left( \frac{8kT}{\pi m} \right)^{1/2} \\ &= (2/\pi)\omega_f / \langle v \rangle / \Delta q \\ &\equiv (2/\pi)\omega_f / \omega_{\text{shuttle}}, \end{aligned}$$

where  $\omega_{\text{shuttle}}$  is the frequency of the particle (group) shuttling between two points  $A$  and  $B$  with an average velocity

$$\langle v \rangle = (8kT/\pi m)^{1/2}.$$

Since  $\omega_f$  is much larger than  $\omega_{\text{shuttle}}$ , the relaxation will be controlled by the second term and we may neglect the first term in such case. Then the relaxation time is of an exponential form. If the shuttling frequency is faster than the vibrational frequency, the energy dissipation is not achieved by the conformational flipping, but is determined mainly by the relaxation of the vibrational motion in a well. This conclusion seems intuitively reasonable.

This aspect of the competition between two different modes of energy dissipation was not considered and is not apparent in the analysis of Heijboer<sup>3</sup>, for instance.

We have not shown the formulas for  $\hat{A}''(\omega)$  and  $\hat{A}'(\omega)$  since it is easy to obtain them. In particular,  $\hat{A}'(\omega)$  can be obtained from  $\hat{A}''(\omega)$ , if the Kramers-Kronig relation<sup>8,15</sup> is made use of.

## 6. CONCLUDING REMARKS

In this article we have proposed to use linear response theory for studying theoretically mechanical energy relaxation phenomena of solid polymer systems at low temperature. We have shown the connection between the linear response theory results and those by Kirkwood who used a different theory. The comparison shows that the present linear response theory can be regarded as being inclusive of Kirkwood's theory. In view of the present lack of adequate general theory, we believe that the present linear response theory approach would be useful for analysis of experimental data in mechanical spectroscopy. The study made here shows that there is a possibility of putting the theory of mechanical spectroscopy perhaps almost on the same level as that of the conventional electromagnetic spectroscopy. This is one of the points the present paper has aimed to make. Due to the inherent complication of polymer systems, interaction between theory and experiment is essential for proper understanding of the physical and mechanical properties of polymers. We hope that we have shown there is a basis for such interaction to begin.

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