

## Neutron Scattering and Collective Oscillation Under Thermal Fluctuation (I)

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In order to evaluate the collective oscillation under thermal fluctuation we developed a computer program to solve the Langevin equation numerically by using the random force. The computer program was applied to a linearly connected collective oscillatory system and the neutron intermediate scattering function and the autocorrelation functions of the velocity and of the position were calculated. This program can be also applied to various problems of dynamics of molecular systems in a potential field under thermal fluctuation.

**KEY WORDS:** Neutron scattering/ Collective oscillation/ Thermal fluctuation/ Langevin equation/ Autocorrelation function/

### I. INTRODUCTION

Neutron scattering is a powerful tool for investigation of molecular dynamics; both normal vibrations and random motions due to thermal fluctuation. The phenomenon by the former is observed as inelastic scattering and that by the latter as quasielastic one. Strictly speaking, these two types of motions cannot be distinguished, especially in disordered materials such as amorphous polymers.<sup>1)</sup> In the extremely low temperature region where thermal fluctuation can be ignored, dynamics of molecular system can be understood in terms of normal vibration concepts even in amorphous materials, though the formalism seems to be very difficult. With increasing temperature, vibrational motions would be damped by thermal fluctuation and at extremely high temperatures it becomes random motion which can be observed as quasielastic scattering. In the intermediate region, the vibrational motions and the random motions are not strictly distinguished.

We developed a computer program to evaluate the collective oscillation under thermal fluctuation and applied this program to a linearly connected collective oscillatory system consisting of  $N$  beads and fixed at both ends. In this paper, preliminary results are reported. The Langevin equation of the system is solved by using the random force and the neutron intermediate scattering function, and the autocorrelation functions of the velocity and of the position are calculated. This model can be applied to local motion of amorphous polymers entangled with each other in the time region  $10^{-13}$  to  $10^{-10}$  sec and the computer program developed can also be applied to various problems of dynamics of molecular systems in a potential field under thermal fluctuation.

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## II. MODEL AND LANGEVIN EQUATION

We consider a model of one-dimensional bead-spring chain consisting of  $N$  beads connected linearly by  $N+1$  harmonic springs of the force constant  $k$ , and all the beads have the same mass  $m$ . Both ends of the chain are fixed. The Langevin equation of the  $i$ -th bead for this system can be written in the following form

$$m \frac{d^2 u_i}{dt^2} + m \gamma_i \frac{du_i}{dt} - f_i = R_i(t) \quad (i=1, \dots, N), \quad (1)$$

where  $u_i$  is the displacement of the  $i$ -th bead from the equilibrium position,  $\gamma_i$  the friction coefficient, and  $f_i$  and  $R_i$  the external force and the random force on the  $i$ -th bead, respectively. It is assumed that the friction coefficient and the random force are the same for all the beads. For the present system, the external force  $f_i$  on the  $i$ -th bead is given by

$$\begin{aligned} f_1 &= k(-2u_1 + u_2), \\ f_i &= k(u_{i+1} - 2u_i + u_{i-1}) \quad (i=2, \dots, N-1), \\ f_N &= k(-2u_N + u_{N-1}). \end{aligned} \quad (2)$$

By the using matrix representation, eq. (1) can be written as

$$m \frac{d^2 \mathbf{u}}{dt^2} + m \gamma \frac{d\mathbf{u}}{dt} - k \mathbf{A} \mathbf{u} = \mathbf{R}(t), \quad (3)$$

where

$$\mathbf{A} = \begin{pmatrix} -2 & 1 & 0 & 0 & \dots & \dots \\ 1 & -2 & 1 & \dots & \dots & \dots \\ 0 & 1 & \dots & \dots & \dots & \dots \\ 0 & \dots & \dots & \dots & 0 & \dots \\ \dots & \dots & \dots & \dots & -2 & 1 \\ \dots & \dots & \dots & 0 & 1 & -2 \end{pmatrix} \quad (4)$$

For the case of  $N=1$ , the system corresponds to a harmonic oscillator under thermal fluctuation. We can analytically calculate some physical quantities of the system of  $N=1$  and we can confirm the validity of the calculation program by comparing the numerical results with the analytical ones.

The random force must be well-defined. Then, we give the following characteristics to the random force;

(i) Ensemble average of  $R(t)$  is zero

$$\langle R \rangle = 0. \quad (5)$$

(ii) Autocorrelation function of  $R(t)$  is given by the Dirac  $\delta$ -function

$$\langle R(0)R(t) \rangle = \langle R^2 \rangle \delta(t), \quad (6)$$

where  $\langle R^2 \rangle$  is the square average of  $R$ .

(iii) Distribution function of the absolute value of  $R(t)$  is assumed to be a Gaussian,

$$g(R) = \frac{1}{\sqrt{2\pi}\sigma} \exp(-R^2/2\sigma^2). \quad (7)$$

(iv) Distribution of the time-interval of  $R(t)$  is defined as

$$f(\tau) = \frac{1}{\alpha} \exp(-\tau/\alpha), \quad (8)$$

where  $\alpha$  is the mean value of the time-interval.

### III. NEUTRON SCATTERING FUNCTION

According to van Hove theory,<sup>2)</sup> the time-space self-correlation function  $G_s(\mathbf{r}, t)$  for the present system can be written as

$$\begin{aligned} G_s(\mathbf{r}, t) &= \langle \rho(0, 0) \rho(\mathbf{r}, t) \rangle \\ &= \frac{1}{N} \left\langle \sum_{i=1}^N \int \delta[\mathbf{r} + \mathbf{r}_i(t') - \mathbf{r}'] \delta[\mathbf{r}' - \mathbf{r}_i(t' + t)] d\mathbf{r}' \right\rangle, \end{aligned} \quad (9)$$

where  $\rho(\mathbf{r}, t)$  is the particle density at a time  $t$  and a position  $\mathbf{r}$  and the bracket  $\langle \rangle$  means an ensemble average. Assuming that there is a particle at an arbitrary time  $t'$  and a position  $\mathbf{r}'$ ,  $G_s(\mathbf{r} - \mathbf{r}', t - t')$  presents the ensemble-averaged probability of finding the same particle at a distant  $\mathbf{r}$  for a later time  $t$ . In thermal equilibrium, the ensemble average does not depend on the time and position origins, so that we can put  $\mathbf{r}' = 0$  and  $t' = 0$ .

The corresponding neutron intermediate scattering function  $I_s(\mathbf{Q}, t)$  is given by

$$\begin{aligned} I_s(\mathbf{Q}, t) &= \langle \rho(0, 0) \rho(\mathbf{Q}, t) \rangle \\ &= \frac{1}{N} \left\langle \sum_{i=1}^N \exp(-i\mathbf{Q}\mathbf{r}_i(0)) \exp(i\mathbf{Q}\mathbf{r}_i(t)) \right\rangle, \end{aligned} \quad (10)$$

where  $\rho(\mathbf{Q}, t)$  is defined as the Fourier transform of  $\rho(\mathbf{r}, t)$  with respect to  $\mathbf{r}$

$$\rho(\mathbf{Q}, t) = \int \rho(\mathbf{r}, t) e^{i\mathbf{Q}\mathbf{r}} d\mathbf{r}. \quad (11)$$

By the Fourier transform of the intermediate scattering function  $I_s(\mathbf{Q}, t)$  with respect to  $t$ , we get the incoherent neutron scattering function  $S_{\text{inc}}(\mathbf{Q}, \omega)$ .

$$S_{\text{inc}}(\mathbf{Q}, \omega) = \int I_s(\mathbf{Q}, t) e^{-i\omega t} dt, \quad (12)$$

where  $\omega$  corresponds to the angular frequency of a scattering particle. In the present report, we solve the Langevin equation [eq. (1)] numerically by using the random force defined by eqs. (5)–(8) and get the time-sequence of the velocities and the positions of the individual scattering particles. Then, the neutron intermediate scattering function can be calculated from the time-sequence and the incoherent neutron scattering function by the Fourier transform of the intermediate one. We average the neutron intermediate scattering function over all the orientation in  $\mathbf{Q}$  space, assuming an isotropic distribution of orientation.

### IV. RESULTS AND DISCUSSION

The autocorrelation function  $\langle R(0)R(t) \rangle$  and the distribution function  $f(\tau)$  of time intervals of the random force used in the present calculation are shown in Fig. 1.

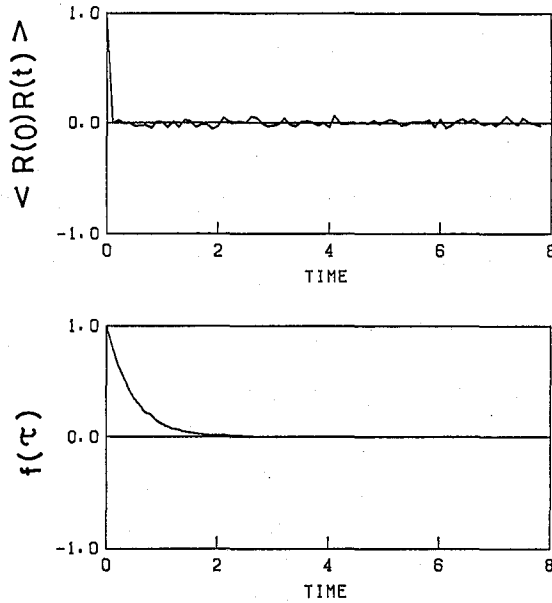


Fig. 1. Autocorrelation function of random force  $\langle R(0)R(t) \rangle$  and distribution function  $f(\tau)$  of time-interval of random force.

$\langle R(0)R(t) \rangle$  can be approximately regarded as the  $\delta$ -function. The time unit in this calculation is arbitrary. All the physical quantities calculated have been obtained from the average over 2000 trials.

We, at first, carry out calculations for a system consisting of one bead  $N=1$  in order to reveal the characteristic properties of the systems and to confirm the validity of the calculation program. The system of  $N=1$  corresponds to a harmonic oscillator under thermal fluctuation with the force constant  $2k$  and mass  $m$ . The autocorrelation functions of the velocity and of the position can be analytically obtained<sup>3)</sup> and we calculate these functions by using the present program to compare them with the analytical ones. It is found that the results obtained by the program agree with the analytical ones within a statistical error. Figure 2 shows the autocorrelation functions of the velocity and of the position and the intermediate neutron scattering function at various values of the friction coefficient. Other parameters such as mass, force constant and mean square value of the random force are fixed. In a low friction limit ( $\gamma^2 \ll k/m$ ), both the velocity autocorrelation function and the position one show a periodic behavior like that of a harmonic oscillator without thermal fluctuation. With increasing the friction coefficient, the velocity autocorrelation function is gradually damped and approaches to the  $\delta$ -function. It is a so-called diffusion-limit. The position autocorrelation function is also damped in the same manner as the velocity autocorrelation function at a value of  $\gamma$  smaller than 1.0. In a large friction limit ( $\gamma^2 \gg k/m$ ), however, it becomes an exponential function in contrast with the velocity autocorrelation function.

Figure 3 shows the autocorrelation functions of the velocity and of the position and the neutron intermediate scattering function for the systems  $N=1, 3, 5, 10, 15$  and 20.

Collective Oscillation under Thermal Fluctuation

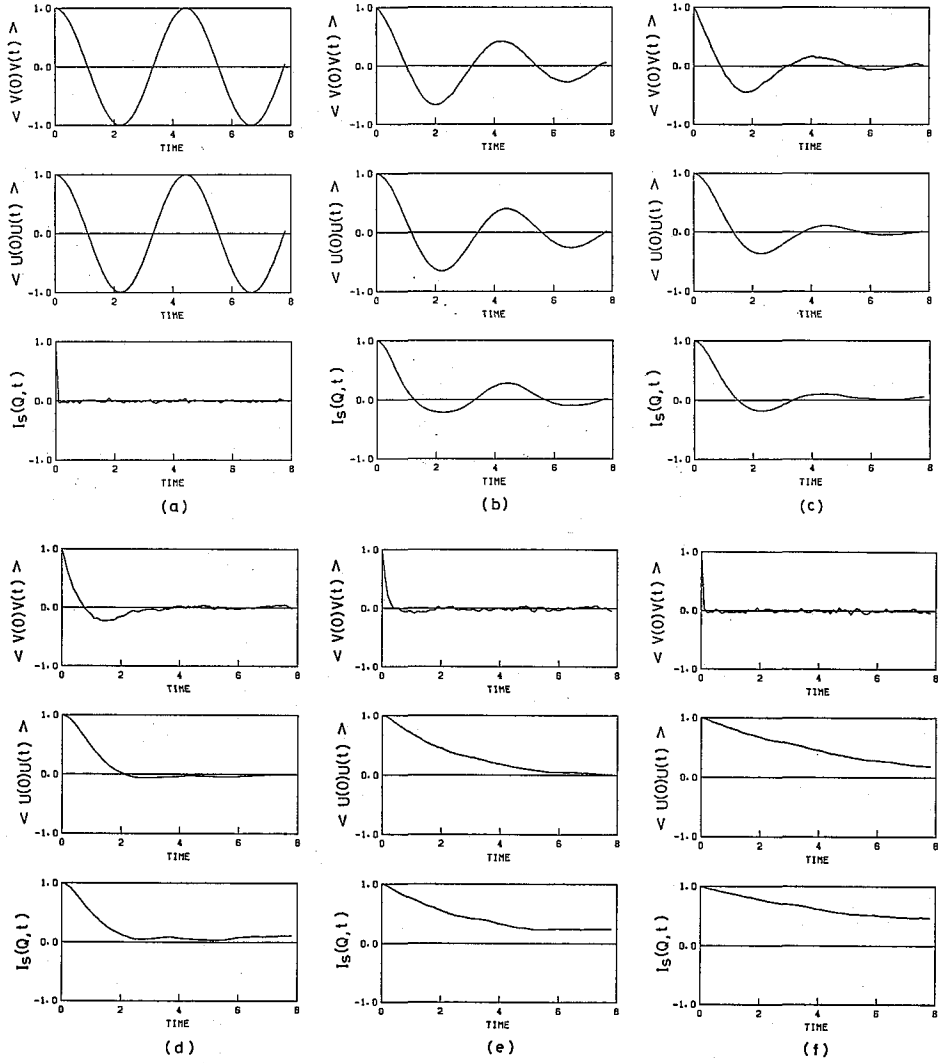


Fig. 2. Velocity and position autocorrelation functions,  $\langle v(0)v(t) \rangle$  and  $\langle u(0)u(t) \rangle$ , and neutron intermediate scattering function  $I_s(Q, t)$  at  $Q=1$ . Friction coefficients; 0.1 (a), 0.5 (b), 1.0 (c), 2.0 (d), 5.0 (e) and 10.0 (f). Both force constant and mass are fixed to be 1.0 for (a)–(f).

The friction coefficient  $\gamma$ , the mass  $m$  and the force constant  $k$  were fixed for all the systems. The velocity autocorrelation function, the position one and the neutron intermediate scattering function of the system  $N=1$  are identical. The velocity autocorrelation function is independent of the number of beads  $N$ , which is determined only by the friction coefficient. On the other hand, the position autocorrelation function and the neutron intermediate scattering function vary with  $N$ . They show a damping oscillation for  $N$  smaller than 5, whereas the oscillatory behavior can be no more observed for  $N$  larger than 10. It means that the restoring force is not effective

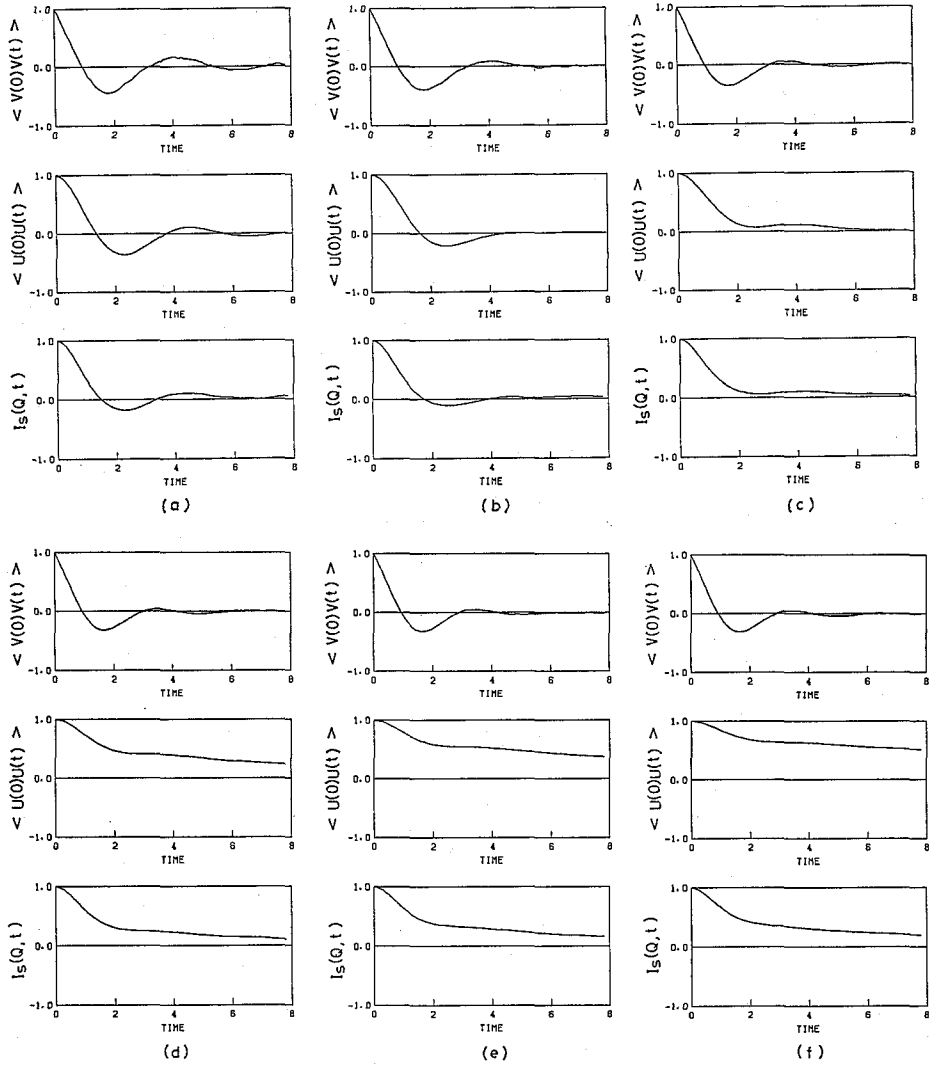


Fig. 3. Velocity and position autocorrelation functions,  $\langle v(0)v(t) \rangle$  and  $\langle u(0)u(t) \rangle$ , and neutron intermediate scattering function  $I_s(Q, t)$  at  $Q=1$  for  $N=1$  (a),  $N=3$  (b),  $N=5$  (c),  $N=10$  (d),  $N=15$  (e) and  $N=20$  (f). Force constant, mass and friction coefficient are fixed to be 1.0 for (a)-(f).

for the long chain.

In other calculations, we have observed the transition from an oscillatory behavior to diffusive one. Such a transition is observed with increasing the friction coefficient, with decreasing the force constant or with increasing the number of beads. It corresponds to the transition from the non-Markov process to Markov one. The transition can be treated by the generalized Langevin equation which was formulated by Mori<sup>4)</sup> and Zwanzig<sup>5)</sup> on the basis of the projection operator method. Inoue has applied it to a random jump particle in the periodic lattice.<sup>6)</sup> In their formalism, the total

information of a molecular system is included in a *memory* function. We will modify the present computer program in order to evaluate the memory function for various molecular systems.

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