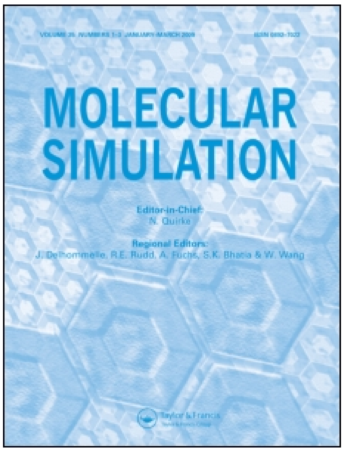

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Fluctuations in Potential and Dynamics of Molecules in Liquids

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FLUCTUATIONS IN POTENTIAL AND DYNAMICS OF MOLECULES IN LIQUIDS

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Results from molecular dynamics of liquid argon and far-infrared spectroscopy of liquid carbon dioxide are compared with those based on a model of a harmonic oscillator undergoing Brownian motion with fluctuations in the spring constant. It is found that both data are fitted well when the friction constant is set zero, indicating that the irreversibility of dynamical behaviour of the liquids arises from fluctuations in potential rather than collisions.

KEY WORDS: Molecular dynamics, far-infrared spectroscopy, liquid carbon dioxide.

Although there are attempts to interpret data on dynamical aspects of molecules in liquids with the help of the generalized Langevin equation, it is not totally without flaws. In fact, Scaife pointed out [1] that results from the generalized Langevin equation do not satisfy causality. Morita [2] examined this view from different standpoints. With this work in mind, we look at data for the velocity correlation function and far-infrared spectrum of non-polar liquid molecules in view of fluctuations in potential. Recent molecular dynamics studies by Tanaka and Ohmine [3] suggest this effect is indeed important in determining dynamic processes of liquid water. In this preliminary report, we investigate the fluctuation by using a simple model of a harmonic oscillator undergoing Brownian motion with fluctuations in spring constant.

On imagining a molecule in a fluid moving under the influence of complicated interactions, we assume in view of the Langevin equation that its motion is given by

$$\ddot{x}(t) + \beta\dot{x}(t) + [\omega^2 + \lambda(t)]x(t) = f(t) \tag{1}$$

In Equation (1), we have taken into account the fact that the molecule collides with surrounding particles through the random force $f(t)$ which is assumed to have properties that $f(t)$ is too random to correlate with any quantity except itself and

$$\langle f(t)\rangle = 0$$

and it is under the influence of the potential

$$V_+(x) = \frac{1}{2}m(\omega^2 + E)x^2$$

or

$$V_-(x) = \frac{1}{2}m(\omega^2 - E)x^2$$

in which $\lambda(t)$ takes E or $-E$ randomly with time t. We suppose that $\lambda(t)$ is a colored dichotomous noise (random square wave) with

$$\langle \lambda(t) \rangle = 0$$

whose correlation function is given by

$$\langle \lambda(t_1)\lambda(t_2) \rangle = E^2 exp(-\gamma|t_1 - t_2|)$$

where $\gamma/2$ represents the average transition frequency for $\lambda(t)$ [4,5].

Equation (1) has been treated by Bourret, Frisch and Pouquet [6] for a different problem to the present one. In this report, we shall re-consider this simple model with a view to understanding the dynamic properties of liquid molecules. Equation (1) also can be regarded as a modification of a parametric oscillation by a stochastic variable $\lambda(t)$, of the damping, and random forces. By taking the Laplace transforms of both sides of Equation (1) with respect to t, we find that

$$\tilde{x}(s) = \int_0^\infty x(t)e^{-st}dt = L[x(t)] = \tilde{g}_x(s) + \tilde{b}(s)L[\lambda(t)x(t)] \tag{2}$$

and

$$\tilde{v}(s) = \tilde{g}_v(s) + \tilde{c}(s)L[\lambda(t)x(t)] \tag{3}$$

where

$$\tilde{g}_x = \tilde{a}(s)x_0 + \tilde{b}(s)[v_0 + \tilde{f}(s)] \tag{4}$$

$$\tilde{g}_v = -\tilde{b}(s)\omega^2 x_0 + \tilde{c}(s)[v_0 + \tilde{f}(s)] \tag{5}$$

in which

$$\tilde{a}(s) = (s + \beta)/\tilde{d}(s) \qquad \tilde{b}(s) = 1/\tilde{d}(s) \qquad \tilde{c}(s) = s/\tilde{d}(s)$$

In the above equations, we have defined

$$\tilde{d}(s) = s^2 + \beta s + \omega^2$$

Equations (2) and (3) may be written

$$x(t) = g_x(t) + \int_0^t b(t-t_1)\lambda(t_1)x(t_1)dt_1 \tag{6}$$

The solution of the integral equation (6) can be expressed as

$$x(t) = g_x(t) + \int_0^t b(t-t_1)\lambda(t_1)g_x(t_1)dt_1 + \int_0^t \int_0^{t_1} b(t-t_1)b(t_1-t_2)\lambda(t_1)\lambda(t_2)g_x(t_2)dt_1 dt_2$$
$$+ \int_0^t \int_0^{t_1} \int_0^{t_2} b(t-t_1)b(t_1-t_2)b(t_2-t_3)\lambda(t_1)\lambda(t_2)\lambda(t_3)g_x(t_3)dt_1 dt_2 dt_3 + \ldots \tag{7}$$

It is obvious from Equations (3) and (7) that

$$v(t) = g_v(t) + \int_0^t c(t-t_1)\lambda(t_1)g_x(t_1)dt_1 + \int_0^t \int_0^{t_1} c(t-t_1)b(t_1-t_2)\lambda(t_1)\lambda(t_2)g_x(t_2)dt_1 dt_2$$
$$+ \int_0^1 \int_0^{t_1} \int_0^{t_2} c(t-t_1)b(t_1-t_2)b(t_2-t_3)\lambda(t_1)\lambda(t_2)\lambda(t_3)g_x(t_3)dt_1 dt_2 dt_3 + \ldots \tag{8}$$

It follows from Equations (4), (5), (7) and (8) that by averaging out over $f(t)$ for $x(t)$ and $v(t)$ on using the assumptions that $\langle f(t) \rangle = 0$, and $f(t)$ does not correlate with any quantity except itself, we see that $f(t)$ can be treated as if $f(t) = 0$, hence

$$G_x(t) = \langle g_x(t)\rangle_f = a(t)x_0 + b(t)v_0 \tag{9}$$

$$G_v(t) = \langle g_v(t)\rangle_f = - b(t)w^2x_0 + c(t)v_0 \tag{10}$$

where $\langle ...\rangle_f$ indicates the average with respect of $f(t)$. It is important to notice that $f(t)$ does not contribute to the determination of $\langle x(t)\rangle$ and $\langle v(t)\rangle$ as long as the above two assumptions are valid, i.e. $f(t)$ could be white as often assumed or colored noise. Now, let us average out $x(t)$ and $v(t)$ over $\lambda(t)$. In view of the relation[2,3]

$$\langle \lambda(t_1)\lambda(t_2)\lambda(t_3) \ldots \lambda(t_n)\rangle = \begin{cases} \langle\lambda(t_1)\lambda(t_2)\rangle\langle\lambda(t_3)\lambda(t_4)\rangle \ldots \langle\lambda(t_{n-1})\lambda(t_n)\rangle & \text{(for even } n\text{)} \\ 0 & \text{(for odd } n\text{)} \end{cases}$$

we find that

$$\langle x(t)\rangle = G_x(t) + E^2\int_0^1\int_0^{t_1} b(t-t_1)b(t_1-t_2)\, exp\,[-\gamma(t_1-t_2)]G_x(t_2)dt_1dt_2$$
$$+ E^4\int_0^t\int_0^{t_1}\int_0^{t_2}\int_0^{t_3} b(t-t_1)b(t_1-t_2)\mathrm{b}(t_2-t_3)b(t_3-t_4)\; exp\,[-\gamma(t_1-t_2+t_3-t_4)]G_x(t_3)dt_1dt_2dt_3dt_4 + \ldots \tag{11}$$

and

$$\langle v(t)\rangle = G_v(t) + E^2\int_0^t\int_0^{t_1} c(t-t_1)b(t_1-t_2)\, exp\;[-\gamma(t_1-t_2)]G_x(t_2)dt_1dt_2$$
$$+ E^4\int_0^t\int_0^{t_1}\int_0^{t_2}\int_0^{t_3} c(t-t_1)bt_1-t_2)b(t_2-t_3)b(t_3-t_4)\, exp\,[-\gamma(t_1 - t_2 + t_3 - t_4)]G_x(t_3)dt_1dt_2dt_3dt_4 + \ldots \quad . \tag{12}$$

Now, on taking the Laplace transform of both sides of Equations (11) and (12), we obtain

$$L[\langle x(t)\rangle] = \frac{\tilde{G}_x(s)}{1 - E^2\tilde{b}(s)\tilde{b}(s+\gamma)} \tag{13}$$

$$L[\langle v(t)\rangle] = \tilde{g}_v + \frac{E^2c(s)\tilde{b}(s+\gamma)\tilde{G}_x(s)}{1 - E^2\tilde{b}(s)\tilde{b}(s+\gamma)} \tag{14}$$

Therefore it follows from Equations (9), (10) and (14) by using the relation:

$$\langle x_0v_0\rangle = 0$$

that

$$L[\langle x(0)x(t)\rangle] = \frac{(s + \text{ß})\tilde{b}(s)\langle x_0^2\rangle}{1 - E^2\tilde{b}(s)\tilde{b}(s+\gamma)} \tag{15}$$

$$L[\langle v(0)x(t)\rangle] = \frac{\tilde{b}(s)\langle v_0^2\rangle}{1 - E^2\tilde{b}(s)\tilde{b}(s+\gamma)} \tag{16}$$

$$L[\langle x(0)v(t)\rangle] = \frac{\tilde{b}(s)\langle x_0^2\rangle[E^2\tilde{b}(s+\gamma) - \omega^2]}{1 - E^2\tilde{b}(s)\tilde{b}(s+\gamma)} \tag{17}$$

$$L[\langle v(0)v(t)\rangle] = \frac{s\tilde{b}(s)\langle v_0^2\rangle}{1 - E^2\tilde{b}(s)\tilde{b}(s+\gamma)} \tag{18}$$

It becomes evident from Equations (16) and (17) that in our model,

$$\langle v(0)x(t)\rangle \neq -\langle x(0)v(t)\rangle \tag{19}$$

except for the case of $E = 0$. This is a contradiction with the usual result for a stationary system.

In obtaining the inverse Laplace transforms of Equations (15)–(18) to express the correlation functions as a function of t, we note that they have the common four simple poles in general. These poles can be found by solving the quartic equation with respect to s,

$$[s(s+\beta)+\omega^2][(s+\gamma)(s+\gamma+\beta)+\omega^2] = E^2$$

There may be the case depending upon the parameters, β, γ, ω^2 and E^2 where the correlation functions to not vanish as $t \to \infty$. This corresponds to the case where at least one of the real part of the solution in the above quartic equation is positive.

To see the effect of fluctuations in potential energy, we compare the velocity correlation function from molecular dynamics of liquid argon with that in Equation (18) in Figure 1. Circles are from the computer simulation of Rahman [7] and the continuous curve represents the theoretical results. To obtain the curve, we have fixed $\gamma = 1$ and changed parameters until the minimum value for the correlation function agrees with the simulation then re-adjusted time scale so as to be identical to the position of the minimum for the simulation result. Values for the parameters shown in Figure 1 and $\omega^2 = 0.5$, $\beta = 0$, and $E^2 = 0.74$ which are normalised with respect to γ. If these are unnormalised, we get $\gamma = 9.83 \times 10^{12}$ sec, $\omega = 6.95 \times 10^{12}$ sec, and $\sqrt{E} = 9.12 \times 10^{12}$ sec. We find it useful to mention that the inverse of $t_{\min}$ which is

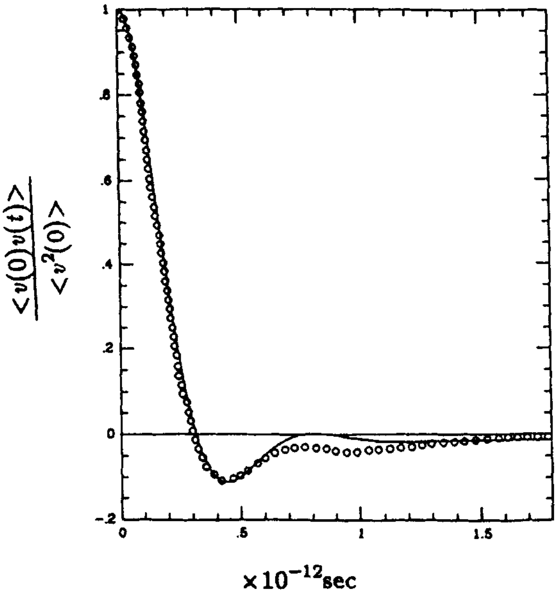

Figure 1 Comparison of normalized autocorrelation function obtained from computer simulation [5] (circles) to the present theoretical result, Equation (18) (continuous curve).

the time when the correlation function takes the minimum value is 2.26×10^{12}sec. We see that the potential changes randomly with the real angular velocity of $\omega + \sqrt{E} = 16.07 \times 10^{12}$sec and the imaginary angular frequency of $|\omega - \sqrt{E}| = 2.17 \times 10^{12}$sec. There will be criticism as to why the potential is allowed to have only two values. In reality, we should consider more values for the potential functuations. We did not do it simply because this would be very difficult. It should be noted that the agreement is particularly good at short time with $\beta = 0$. Non-zero β gives fast decay in the short time whereas the oscillator without the fluctuation of the potential ($E = 0$) does not lead to the observed behaviour after the minimum.

Now, let us interpret the far infrared spectrum of non-polar molecules based on the present model. For the sake of simplicity we ignore the rotational contribution. We see that an induced dipole arises from fluctuations in potential resulting from the random change in the environment. We must be careful here to use Kubo's linear response theory to evaluate the spectrum because of the relation in (19), although the dipole correlation has been obtained already in Equation (15). We have to start from the beginning to avoid all the ambiguities. If we apply an electric field $E_0\cos\Omega t$ to the system, the equation of motion in Equation (1) must be modified as given by

$$\ddot{x}(t) + \beta\dot{x}(t) + [\omega^2 + \lambda(t)]x(t) = qE_0\cos\Omega t + f(t) \tag{20}$$

where q is an electric charge resulting in the induced dipole. The above procedures in obtaining Equation (13) can be employed to lead to

$$L[\langle x(t)\rangle] = \frac{\tilde{G}_q(s)}{1 - E^2\tilde{b}(s)\tilde{b}(s+\gamma)} \tag{21}$$

where

$$\tilde{G}_q = \tilde{a}(s)x_0 + \tilde{b}(s)\left[v_0 + \frac{qE_0}{2}\left(\frac{1}{s - i\Omega} + \frac{1}{s + i\Omega}\right)\right] \tag{22}$$

On considering how Equation (21) can be inverted to obtain $\langle x(t)\rangle$ in the limit of $t \to \infty$, and on confining ourselves to the region where all the transient effects vanish as $t \to \infty$, we see that the poles contribute to $\langle x(t)\rangle$ are just $s = i\Omega$ and $s = -i\Omega$, thus finding that aside from a normalization constant, the term responsible for the dielectric loss is

$$\operatorname{Im}\left[\frac{\tilde{b}(i\Omega)}{1 - E^2\tilde{b}(i\Omega)\tilde{b}(i\Omega)\tilde{b}(i\Omega + \gamma)}\right] \tag{23}$$

Thus, the correlation function responsible for the far infrared spectrum is in fact$\langle v(0)x(t)\rangle$ in Equation (16) in the present case. In Figure 2, the experimental spectrum of carbon dioxide measured by Birnbaum, Ho and Rosenberg [8] is compared with the theoretical one (fine curve). In obtaining the latter, as in the case of velocity correlation function, $\gamma = 1$ is fixed and the position of the maximum of the spectrum is always set identical to the experimental value. The normalised parameters with respect to γ we obtained are $\omega^2 = 0.25$, $\beta = 0.0$ and $E^2 = 0.25$. As before, if these are unnormalised, we find $\gamma = 7.18 \times 10^{12}$sec, $\omega = 3.59 \times 10^{12}$sec, and

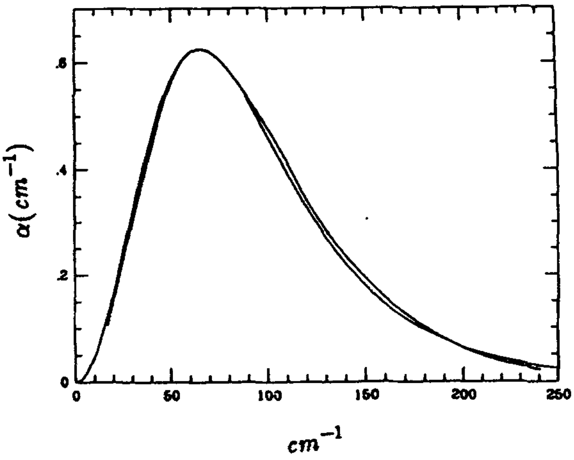

Figure 2 Comparison of the experimental far infra-red spectrum of liquid carbon dioxide [6] (bold curve) to that of the present result (fine curve).

$\sqrt{E} = 5.08 \times 10^{12}$sec. The maximum of the absorption is at 65.11 cm^{-1}. It is again noted that $\beta = 0$ gives the best fit. We see that fluctuations in the potential energy accounts for the dynamic behaviour of simple liquids in terms of velocity and dipole response functions. But both functions are not very sensitive to the random force $f(t)$. In addition, $\beta = 0$ means that contribution from $f(t)$ is negligibly small in determining the velocity and dielectric responsible functions of simple liquid molecules. In this sense, the far infrared spectra of nonpolar liquids should be appropriately called potential fluctuation-induced spectra rather than collision-induced. The full treatment of the present model will be found elsewhere in the future.

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