Generalized nonlinear Langevin equation for a rotor

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A pendulum (rotor) coupled to a bath of harmonic oscillators is set up as a model for the dynamics of strongly coupled systems. The oscillators can be eliminated from the equation of motion for the rotor, except for initial conditions. The resulting Langevin equation is exact. Numerical solutions are provided for the power spectra of velocity and angular correlation functions of the pendulum for a broad range of the strength of the coupling starting from a weak coupling (hindered rotor) to the strong-coupling ("free" rotor) limit, using both the rotor equation of motion and the full molecular dynamics.

There has been considerable interest lately in the dynamics of a damped driven pendulum. It serves as a model system for the Josephson junction[1] and the rotational relaxation of molecules,[2] among other things. These studies are based on the Langevin equation in which the effect of the thermal bath on the pendulum is taken into account through position and frequency independent damping and random force terms. In the present study we have been partially motivated by the example of the CN^- molecular ion in alkali halide crystals, particularly in KBr.[3] In this case there is a strong coupling between the rotating molecule[4,5] and the surrounding ions. Following Caldeira and Leggett[6] we shall represent this environment, the polarizable lattice, by a set of harmonic oscillators. We shall not assume however, contrary to the usual practice, that the actual equations of motion of the pendulum can be replaced by a Langevin equation or by some approximation to the Mori theory.[4,5,7] Thus we derive and solve exactly, albeit numerically, a strong coupling nonlinear dynamic problem in classical statistical mechanics.

The Lagrangian of our model is

$$L=\frac{I}{2}\dot{\theta}^2+D\cos\theta+\sum_{i=1}^{N}\left[\tfrac{1}{2}M_i\dot{x}_i^2-\tfrac{1}{2}K_i x_i^2+\frac{A_i}{\sqrt{N}}x_i\sin\frac{\theta}{2}\right], \tag{1}$$

where θ is the pendulum angle, and the x_i's are the coordinates of N oscillators. In a molecular rotor realization of this model one would use $\theta=M\phi$ for an M-fold cosine potential. The interaction with the oscillators has such a form that the customary displaced oscillator transformation would also yield a potential of the form of $\cos\theta$ and could be used to cancel the rigid potential in whole or in part. We introduce a quantity analogous to a polaron activation energy

$$W_A=\frac{1}{N}\sum_i A_i^2/4K_i\ , \tag{2}$$

the dimensionless coupling constant $\alpha=W_A/D$, and the dimensionless time $\tau=\omega_D t$, where ω_D is the Debye frequency associated with the oscillators. In addition, we define the dimensionless frequency $\Omega_i=\omega_i/\omega_D$, coordinates $X_i=\sqrt{M_i/D}\,\omega_D x_i$, velocities $\dot{X}_i=dX_i/d\tau$, and moment of inertia of the rotor $\mu=I\omega_D^2/D$. In terms of these dimensionless quantities the equations of motion can be written as

$$\mu\ddot{\theta}+\sin\theta-\sqrt{\alpha/N}\sum_i\Omega_i X_i\cos\frac{\theta}{2}=0\ , \tag{3}$$

$$\ddot{X}_i+\Omega_i^2X_i-2\sqrt{\alpha/N}\,\Omega_i\sin\frac{\theta}{2}=0\ , \tag{4}$$

where we have assumed A_i^2/K_i to be independent of i. The harmonic oscillator equations can now be solved and their coordinates substituted in the rotor equation.[8] For the former we use the two-dimensional Debye density of states, i.e.,

$$\rho(\Omega)=2\Omega,\quad 0\le\Omega\le1\ , \tag{5}$$

and obtain

$$\mu\ddot{\theta}(\tau)+\sin\theta(\tau)-2\alpha\cos\frac{\theta(\tau)}{2}\int_0^\tau K(\tau-\tau')\sin\frac{\theta(\tau')}{2}d\tau'-\sqrt{\alpha/N}\cos\frac{\theta(\tau)}{2}\sum_i[\Omega_iX_i(0)\cos\Omega_i\tau+\dot{X}_i(0)\sin\Omega_i\tau]=0\ , \tag{6}$$

where the kernel K for $N\to\infty$ is given by

$$K(\tau)=2\int_0^1 d\Omega\,\Omega^2\sin\Omega\tau\ . \tag{7}$$

The sum in the last term of Eq. (8) cannot be replaced by an integral because it is over the initial values of the oscillator positions and velocities and these are chosen randomly from an initial thermal distribution at a dimensionless temperature $T^*=k_BT/D$.

Integrating the third term of Eq. (6) by parts we can rewrite it as a generalized nonlinear Langevin equation[9]

$$\mu\ddot{\theta}+(1-\alpha)\sin\theta(\tau)+\alpha\cos\frac{\theta(\tau)}{2}\int_0^\tau H(\tau-\tau')\cos\frac{\theta(\tau')}{2}\dot{\theta}(\tau')d\tau'-\sqrt{\alpha}\cos\frac{\theta(\tau)}{2}F(\tau)=0\ , \tag{8}$$

where

$$H(\tau)=2\int_0^1 d\Omega\,\Omega\cos(\Omega\tau) \tag{9}$$

and

$$F(\tau)=\frac{1}{\sqrt{N}}\sum_i[\Omega_iX_i(0)\cos(\Omega_i\tau)+\dot{X}_i(0)\sin(\Omega_i\tau)]\ . \tag{10}$$

The initial conditions for the rotor are invariably chosen as $\theta(0)=0$ and $\dot{\theta}(0)=0$. This choice gets rid of a transient that would otherwise appear in Eq. (8). The rigid force gets renormalized to $(1-\alpha)\sin\theta(\tau)$. Thus, $\alpha=1$ corresponds to a "free" rotor. The last term represents a force which is deterministic in time after the initial conditions have been chosen randomly.

We have solved Eq. (6) on a CDC Cyber 170 Model 750 mainframe computer for the parameter values $\alpha=0.01$, 0.1, 1, $\mu=1$, 0.25, 4.0, and $T^*=1.0$, 0.5, 0.1. In each case the Debye period was subdivided into 60 steps and a total of 43 Debye cycles were run for each of 10 different seeds, i.e., for 10 different sets of initial values of $X_i(0)$ and $\dot{X}_i(0)$ for $N=1000$ oscillators. Power spectra for $\sin(\theta/2)$, $\cos(\theta/2)$ and of the angular velocity $\dot{\theta}$ [denoted by $P_s(\Omega)$, $P_c(\Omega)$, and $P_v(\Omega)$, respectively], were calculated over the last 28 cycles and averaged over the 10 seeds. We checked the equipartition theorem for the rotational kinetic energy being satisfied over these cycles and found reasonably good results only for $\mu=1$ and $\alpha\neq0$. For the uncoupled rotor, $\alpha=0$, the small amplitude oscillation frequency is $\Omega_c=\sqrt{\mu}$. Ω_c is equal to the Debye frequency for $\mu=1$ and this value of μ allows for effective dynamic coupling to most degrees of freedom. We therefore report results for this value of μ only. Figure 1(a) shows $P_v(\Omega)$ for $T^*=1.0$ and $\alpha=0.01$, 0.1, and 1. For weak coupling $\alpha=0.01$, $P_v(\Omega)$ shows high-frequency peaks corresponding to oscillatory motion inside the well and a low-frequency peak arising from motion over the barrier taking place over longer periods. This interpretation of the low-frequency peak is confirmed by examining Fig. 2 which shows $P_v(\Omega)$ for $T^*=0.5$. The low-frequency peaks for $\alpha=0.01$ and 0.1 are strongly suppressed. Returning to Fig. 1, (b) and (c) give $P_s(\Omega)$ and $P_c(\Omega)$, respectively. The results confirm what one expects from the Mori theory[5] for small α, namely that the sine shows an oscillator and the cosine a central peak (the

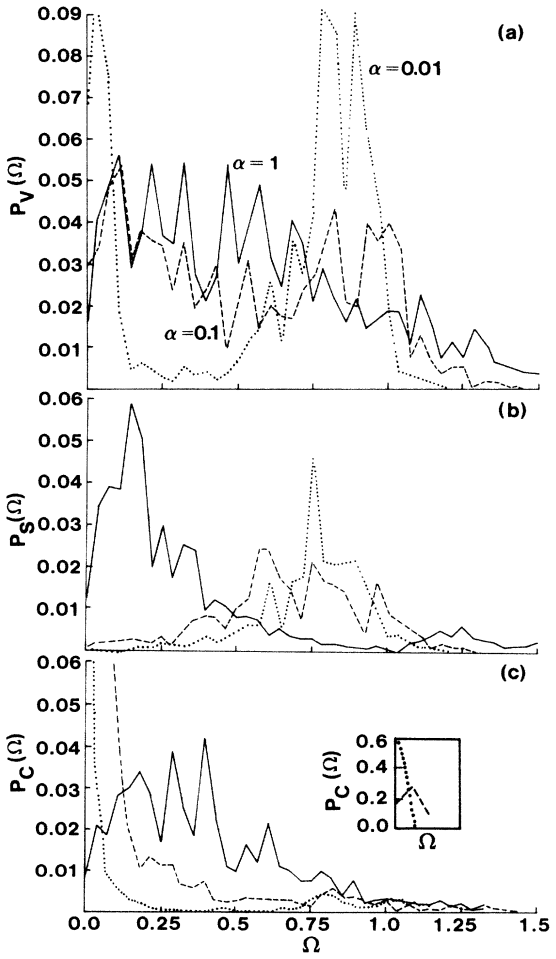

FIG. 1. Frequency dependence of the power spectrum of (a) angular velocity $[P_v(\Omega)]$, (b) $\sin(\theta/2)$ $[P_s(\Omega)]$; and (c) $\cos(\theta/2)$ $[P_c(\Omega)]$ for (solid line) $\mu=1$, $T^*=1$, and $\alpha=1$, 0.1 (dashed line), and 0.01 (dotted line).

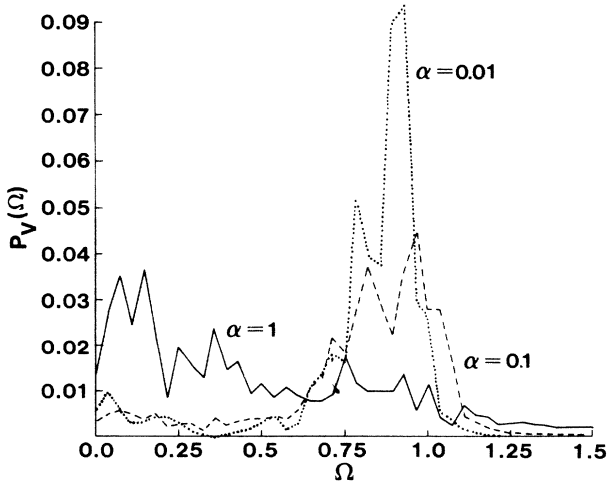

FIG. 2. Frequency dependence of the power spectrum of velocity $P_v(\Omega)$ for $\mu=1$, $T^*=0.5$. See Fig. 1 caption for detail.

latter also shows a weak high-frequency peak). Increasing α to 0.1, the general character of the curves does not change, but the peaks broaden. For $\alpha=1$, both $P_s(\Omega)$ and $P_c(\Omega)$ show qualitatively similar frequency dependence.

Figure 3 shows the results for $\alpha=1$ for three values of the temperature T^*, namely, 0.1, 0.5, and 1. For this case the equilibrium expectation values of $\sin^2(\theta/2)$ and $\cos^2(\theta/2)$ can be shown to be equal. This result is confirmed by numerically integrating $P_s(\Omega)$ and $P_c(\Omega)$ over all frequencies. Thus in this sense the rotor is "free." However, $P_s(\Omega)$ and $P_c(\Omega)$ differ considerably in their frequency dependence. For $T^*=0.1$ the motion of the rotor is slow; both $P_s(\Omega)$ and $P_c(\Omega)$ are large at small frequencies. The results are near the adiabatic limit, i.e., $\theta=0$. With increasing temperature the low-frequency peaks of $P_s(\Omega)$ and $P_c(\Omega)$ broaden and $P_s(\Omega)$ acquires a small high-frequency peak. $P_v(\Omega)$ is broad at all temperatures (with some indication of two peak structure) which suggests, at least roughly, that a central peak with a temperature independent damping constant may describe the dynamics. It is to be noted, however, that the $P_v(\Omega)$ in all figures has a minimum at zero frequency. This may be

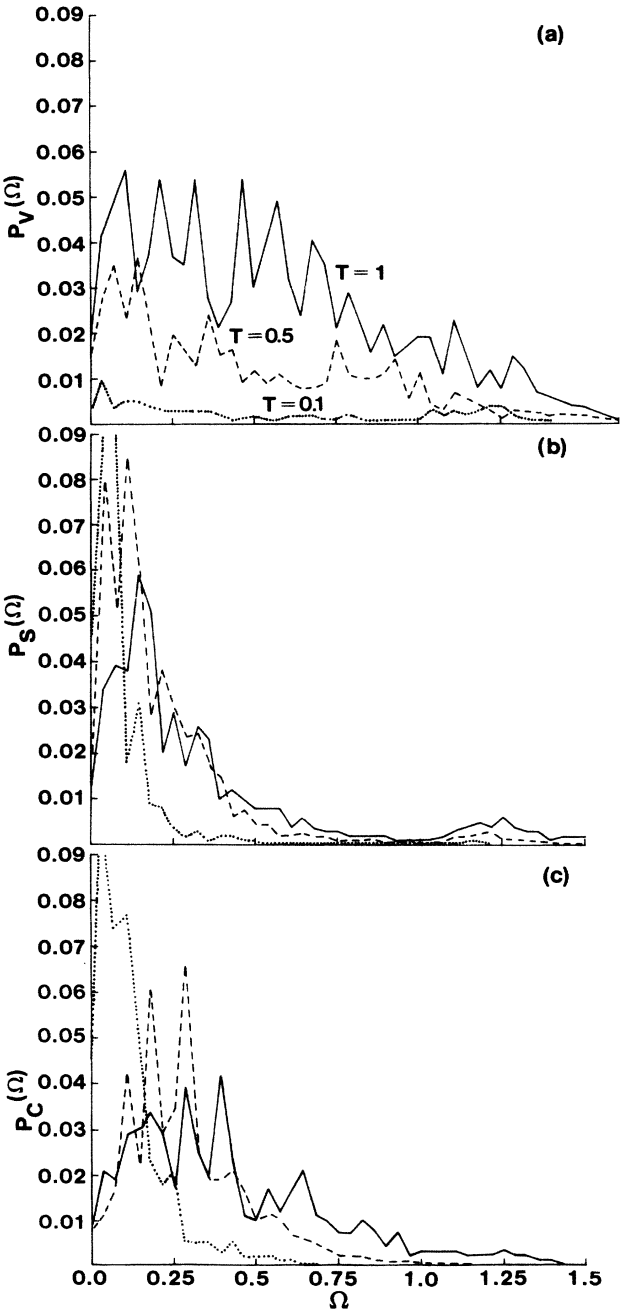

FIG. 3. Frequency dependence of the power spectrum of (a) angular velocity $[P_v(\Omega)]$, (b) $\sin(\theta/2)$ $[P_s(\Omega)]$, and (c) $\cos(\theta/2)$ $[P_c(\Omega)]$ for (solid line) $\mu=1$, $\alpha=1$, and $T^*=1$, 0.5 (dashed line), and 0.1 (dotted line).

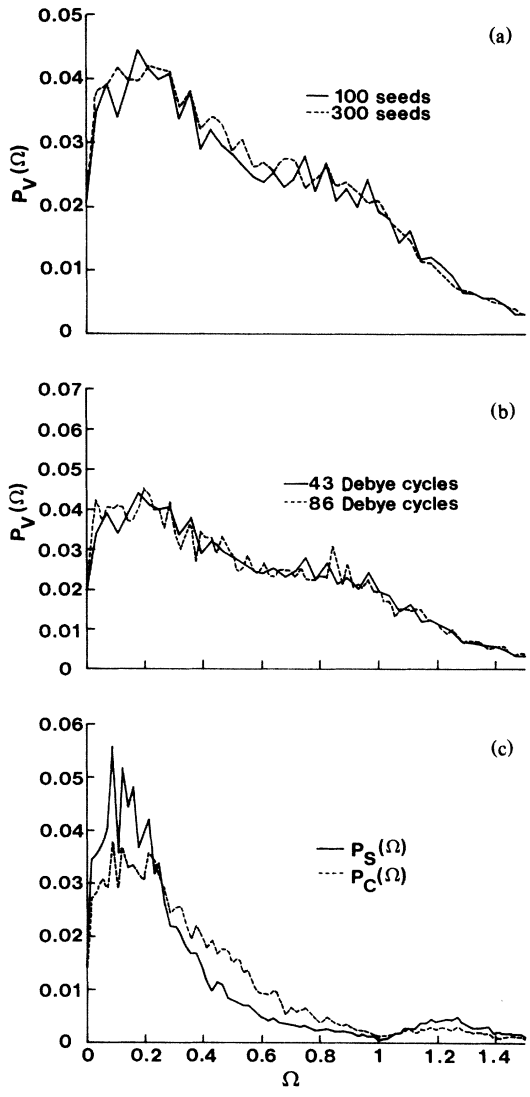

FIG. 4. Frequency dependence of the power spectrum of angular velocity $[P_v(\Omega)]$ (a) for 100 seeds (solid line) and 300 seeds (dashed line) for 43 Debye cycles and (b) for 100 seeds and for 43 Debye cycles (solid line) and 86 Debye cycles (dashed line). (c) Frequency dependence of the power spectrum $P_s(\Omega)$ (solid line) and $P_c(\Omega)$ (broken line) for 100 seeds and 86 Debye cycles. $\mu=1$, $T^*=1$, and $\alpha=1.0$.

ascribed to the Debye spectrum of the bath of oscillators. In fact, for a free particle whose dynamics is governed by the usual Langevin equation (frequency independent damping) the spectrum of velocity autocorrelation function is directly related to the spectrum of the bath oscillators[10] and $P_v(0)=0$ for a two-dimensional Debye spectrum. However the low-frequency behavior of $P_v(\Omega)$ in the present model will be affected strongly by the frequency dependence of damping and the nonlinear coupling between the rotor and the bath oscillators and the correct Ω dependence of $P_v(\Omega)$ as $\Omega \rightarrow 0$ needs further careful study.

In our earlier paper[5] we investigated the effect of translation-rotation coupling on CN^- in KBr based on the Mori theory using the approximation scheme of de Raedt and Michel.[7] We found in the range of low barriers that the correlation functions for E_g and T_g symmetries in a cubic potential [which correspond here to $\cos(\theta/2)$ and $\sin(\theta/2)$, respectively] both had a central peak when the temperature was of the order of the barrier height. There was some doubt as to the validity of this result because the oscillator dynamics was not fully handled in this approximation. Our present results suggest (although the calculations were carried out for a model two-dimensional system) that this approximation is reasonable in the low-frequency region because in the $\alpha=1$ case we obtain low-frequency peaks both for $P_s(\Omega)$ and $P_c(\Omega)$.

To test the general conclusions discussed above, we have performed full molecular dynamics (MD) calculations for the system using Eqs. (3) and (4) with $\alpha=T^*=\mu=1$. These were done on an IBM PC with a 8087 Math Coprocessor. The program used for these calculations were written in Microsoft FORTRAN, version 3.3 and ran a factor of 15 times slower than an identical program run on the mainframe computer used for the original limited (only the central rotor) MD calculations. In order that the computer runs take a reasonable length of time, we reduced the number of bath oscillators to 100. To compensate for this we increased the number of seeds. Figure 4(a) shows the results for P_v for 43 Debye cycle runs with 100 and 300 seeds. In general the curve for 300 seeds is slightly smoother than that for 100 seeds, especially in the low-frequency range. More importantly however, both follow the same general trend encouraging us that 100 seeds provides a sufficient "sample" of ensembles for these simulations. To check for equilibration of the rotor we ran the system twice as long (86 Debye cycles with the transforms calculated over the last 56 cycles) for the same number of oscillators, identical initial conditions and 100 seeds. The results for P_v are shown in Fig. 4(b). Although somewhat noisier than the curve for 43 Debye cycles, the 86 Debye cycle result once again follows the same trend giving us further confidence that at least the gross features of the equilibrium system have been correctly determined. By comparing the solid line in Fig. 4(b) with the $T=1.0$ curve in Fig. 3(a) we find the noise has been significantly reduced even with the smaller number of oscillators, suggesting that the number of seeds is a more important factor than the number of oscillators in determining the precision of the results. Finally, in Fig. 4(c) we show the results for $P_c(\Omega)$ and $P_s(\Omega)$ for the 86 Debye cycle runs. Note that they both show the same general structure (although P_c is slightly broader), as would be expected for a nearly "free" rotor ($\alpha=1$). By comparing these with the corresponding curves in Figs. 3(b) and (c) we once again see that the noise has been reduced. We also note that the zero-frequency minimum and the high-frequency peak persist in Fig. 4(c). We are presently performing additional calculations for different temperatures, coupling constants and values of μ. We will present these results and further interpretation of the data in a later paper.

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