ELSEVIER

Journal of Molecular Structure (Theochem) 361 (1996) 111–116

THEO CHEM

Nosé–Hoover dynamics of a nonintegrable hamiltonian system

Shrish Tiwari, Ramakrishna Ramaswamy*

School of Physical Sciences, Jawaharlal Nehru University, New Delhi 110 067, India

Received 3 April 1995; accepted 7 April 1995

Abstract

We study the dynamics of a hamiltonian system with two degrees of freedom coupled to a Nosé–Hoover thermostat. In the absence of the thermostat, the system is quasi-integrable: at low energies, most of the motion is on two-dimensional tori, while at higher energies, the motion is mainly chaotic. Upon coupling to the thermostat the system becomes more chaotic, as evidenced by the magnitude of the largest Lyapunov exponent. In contrast to the case of isotropic oscillator systems coupled to thermostats, there is no evidence for a regime of integrable behaviour, even for large values of Q.

1. Introduction

Molecular dynamics simulations of many-particle systems [1] at constant temperature have been greatly facilitated by the introduction, in the mid-1980s, of the Nosé–Hoover thermostat [2]. This scheme, which yields the deterministic equations of motion, results from the assumption that the system is coupled to a specially chosen additional degree of freedom. A number of studies [2–4], have shown that this gives rise to canonical distributions in the phase-space if the dynamics of the extended system (i.e. the system of interest + the thermostat) is ergodic.

The incorporation of the Nosé equations in the dynamics is guaranteed [2,5] to give a canonical distribution in the system of choice, and accordingly, a number of applications have been made in diverse areas [6–8], since comparison with experimental results is direct. However, study of the intrinsic dynamics of the Nosé equations for systems with few degrees of freedom is also important [3,4,9], since the question of ergodicity in the extended system has not been examined in detail.

In this paper we study the Nosé–Hoover dynamics of a system with two degrees of freedom. The isolated system is a perturbed isotropic oscillator which is intrinsically quasi-integrable [10]: at low energies, the dynamics are regular and lie on the surface of two-dimensional invariant tori in the phase space. At higher energies, these tori are destroyed by the perturbation, as described by the Kolmogorov–Arnold–Moser (KAM) theory [10,11]. The chaotic nature of the system dynamics can be characterised by the largest Lyapunov exponent; there is a "transition" [11] to large-scale chaos at a well-defined energy. (This behaviour is typical of coupled oscillator systems, and the phenomenology has been described in detail for the similar Hénon–Heiles hamiltonian [12]. This latter system is unfortunately only quasibound, and is thus somewhat more difficult to study in

* Corresponding author.

SSDI 0166-1280(95)04309-8

the present context, since at any nonzero temperature, some of the motion is unbounded.)

Upon addition of the thermostat, although comparison with constant energy studies is no longer direct, we can make correspondence with the "most probable" energy shell. We find that the largest Lyapunov exponent of the extended system can be significantly enhanced, depending on the value of the parameter Q that characterises the thermostat [2].

The Nosé–Hoover prescription is simple to describe. Given a dynamic system with N freedoms, described by a hamiltonian $H_s = \sum_{i=1}^{N} p_i^2/m_i + V(\vec{q})$, where V is the interaction potential and $\vec{q}$ and $\vec{p}$ are the coordinates and conjugate momenta, respectively, the Nosé–Hoover equations of motion are obtained by introducing an additional degree of freedom, ζ, which is coupled to the motion of the system through

$$\dot{q}_i = \frac{\partial H}{\partial p_i} = p_i/m_i \tag{1}$$

$$\dot{p}_i = -\frac{\partial H}{\partial q_i} - \zeta p_i = -\frac{\partial V}{\partial q_i} - \zeta p_i \qquad i = 1 \dots N \tag{2}$$

The evolution of the fictitious heat-bath variable ζ, and its conjugate coordinate, s, is governed by

$$\dot{\zeta} = \frac{1}{Q}\sum_{i=1}^{N}\left(p_i\frac{\partial H}{\partial p_i} - k_B T\frac{\partial p_i}{\partial p_i}\right) = \frac{1}{Q}\left(\sum_{i=1}^{N}\frac{p_i^2}{m} - Nk_B T\right) \tag{3}$$

$$\dot{s} = s\zeta \tag{4}$$

where T is the temperature and $1/Q$ corresponds to the "mass" of the heat-bath. The extended system is thus described by the effective hamiltonian

$$H_e = H_s + \zeta^2/2(1/Q) + Nk_b T \log s \tag{5}$$

which is conserved by the dynamics.

A detailed study on the effect of the thermostat on the integrable N-dimensional isotropic harmonic oscillator has been recently carried out by Nosé [9]. Depending on the initial conditions and on the parameter Q, the system shows a quasiperiodic behaviour of the actions. Although the extended system is, strictly speaking, nonintegrable, in the large Q limit the system appears to be integrable, and does not show evidence of ergodicity, even after coupling to the heat-bath. However, nonergodicity appears to be exceptional behaviour: once the degeneracy in the oscillator frequencies is broken, the N-dimensional harmonic oscillator system is ergodic [9].

In the present work we retain the degeneracy in the oscillator frequencies and instead examine the effect of a nonintegrable perturbation. Upon addition of this term, the system hamiltonian becomes

$$H_s = \tfrac{1}{2}(p_1^2 + p_2^2 + q_1^2 + q_2^2) + \alpha q_1^2 q_2^2 = H_0 + \alpha H_1 \tag{6}$$

where α is the strength of the nonintegrable perturbation. In the absence of the thermostat, the dynamics of this system, which were originally examined by Pullen and Edmonds [13], has been studied extensively and can be summarised as follows. At low energies, $E < 10$, this system shows regular orbits for almost all initial conditions, while at high energies $E \geqslant 50$, virtually all the tori have collapsed and most of the phase space is covered with chaotic trajectories. At intermediate energies, there are KAM surfaces and islands of regular behaviour in the stochastic sea, as is typical in quasi-integrable systems [11]. Since the unthermostatted system is itself intrinsically chaotic, we expect thermalisation to be more effective, even for fairly large values of Q. Since most dynamic systems, and in particular those describing many-particle systems, are nonlinear and in all likelihood, nonintegrable, this would suggest that the Nosé–Hoover methodology is reliable in most applications.

This paper is organised along the following lines. We apply the methods of analysis introduced for the isotropic (integrable) harmonic oscillator to the nonintegrable case in order to assess the speed of thermalisation in the latter system. This is described in Section 2. Since the equations of motion are deterministic, it is possible to define the Lyapunov exponents of the extended dynamic system. These are evaluated in Section 3, as a function of temperature, and comparison is made with constant energy (microcanonical) studies. A summary and discussion of our results is given in Section 4.

2. Thermalisation

In this Section we study the effect of the nonintegrable perturbation on the process of thermalisation. For the isotropic oscillator case, it has been observed [9] that the motion in the extended system is quasiperiodic, with a beat frequency Ω that varies as $1/Q$. The quasiperiodicity was seen in the time-dependence of the energy or action in each of the degrees of freedom. Upon addition of the nonintegrable term, identification of this phenomenon is facilitated by transforming the system using the set of action angle variables provided by the isotropic oscillator,

$$J_i = \frac{1}{2}(p_i^2 + q_i^2) \tag{7}$$

$$\theta_i = \tan^{-1}\left(\frac{q_i}{p_i}\right) \qquad i = 1,2 \tag{8}$$

Since $\omega_1/\omega_2 = 1$ a further canonical transformation through an F_2-generating function is appropriate,

$$F_2 = (\theta_1 - \theta_2)\hat{J}_1 + \theta_2\hat{J}_2 \tag{9}$$

which transforms from $\vec{J}$, $\vec{\theta}$ to $\vec{\hat{J}}$, $\vec{\hat{\theta}}$, where $\hat{\theta}_1 = \theta_1 - \theta_2$. Applying this to H_s and averaging over $\hat{\theta}_2$, we obtain the transformed system hamiltonian as

$$\bar{H}_s = \hat{J}_2 + \alpha\hat{J}_1(\hat{J}_2 - \hat{J}_1)(1 + \tfrac{1}{2}\cos 2\hat{\theta}_1) \tag{10}$$

Upon incorporation of the thermostat, the Nosé equations of motion in these variables are

$$\begin{aligned}\dot{\hat{J}}_1 = & -2\zeta\hat{J}_1\cos^2(\hat{\theta}_1 + \hat{\theta}_2) \\ & -4\alpha\hat{J}_1(\hat{J}_2 - \hat{J}_1)\sin 2(\hat{\theta}_1 + \hat{\theta}_2)\sin^2\hat{\theta}_2\end{aligned} \tag{11}$$

$$\begin{aligned}\dot{\hat{J}}_2 = & -2\zeta[\hat{J}_1\cos^2(\hat{\theta}_1 + \hat{\theta}_2) + (\hat{J}_2 - \hat{J}_1)\cos^2\theta_2] \\ & -4\alpha\hat{J}_1(\hat{J}_2 - \hat{J}_1)[\sin 2(\hat{\theta}_1 + \hat{\theta}_2)\sin^2\hat{\theta}_2 \\ & +\sin^2(\hat{\theta}_1 + \hat{\theta}_2)\sin^2\hat{\theta}_2]\end{aligned} \tag{12}$$

$$\begin{aligned}\dot{\hat{\theta}}_1 = & \zeta[\sin(\hat{\theta}_1 + \hat{\theta}_1)\cos(\hat{\theta}_1 + \hat{\theta}_2) - \sin\hat{\theta}_2\cos\hat{\theta}_2] \\ & +4\alpha[(\hat{J}_2 - 2\hat{J}_1)\sin^2(\hat{\theta}_1 + \hat{\theta}_2)\sin^2\hat{\theta}_2]\end{aligned} \tag{13}$$

$$\dot{\hat{\theta}}_2 = 1 + \zeta\sin\hat{\theta}_2\cos\hat{\theta}_2 + 4\alpha\hat{J}_1\sin^2(\hat{\theta}_1 + \hat{\theta}_2)\sin^2\hat{\theta}_2 \tag{14}$$

$$\dot{\zeta} = \frac{1}{Q}[2\hat{J}_1\cos^2(\hat{\theta}_1 + \hat{\theta}_2) + 2(\hat{J}_2 - \hat{J}_1)\cos^2\hat{\theta}_2 - gT] \tag{15}$$

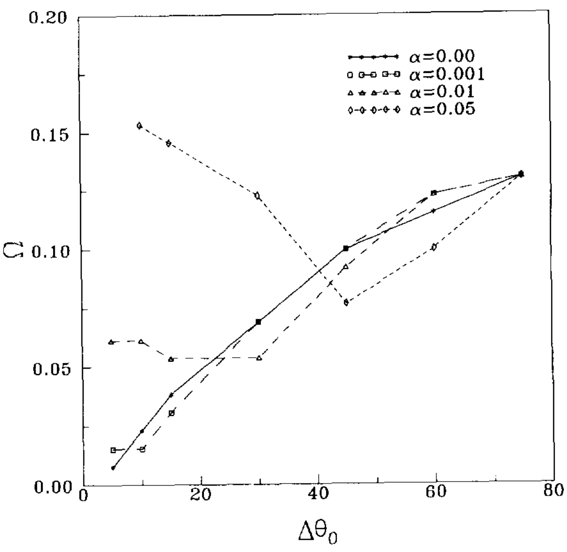

Fig. 1. Variation of the beat frequency, Ω, with respect to the difference in initial conditions, $\Delta\theta_0$, for different values of the nonlinear coupling constant, α.

Note that the equation of motion for s, the variable conjugate to ζ is unimportant for the evolution of the remaining variables, and we work in units of $k_B = 1$.

These equations are integrated for differential initial conditions $\Delta\theta_0$, and for different values of α, and results are shown in Fig. 1. For $\alpha = 0$, the variation of the beat frequency, Ω, is well described by the curve $\Omega = A\sin(\Delta\theta_0)$, with $A = 0.136$, and for sufficiently small values α (say <0.001) this dependence of the beat frequency on $\Delta\theta_0$ remains. For larger values of the nonlinearity, however, there is a marked deviation, specially for low initial phase difference $\Delta\theta_0$ values: the beat frequency for the nonintegrable system turns out to be much larger. Since the beat frequency is a measure of rapidity of thermalisation, the present results reveal that the nonlinear system thermalises faster than the integrable system. The contrast is greatest in the regime where the unperturbed system is regular.

The mechanism of thermalisation in the extended system is the frequent change in the *energy shell* occupied by the trajectory of the dynamic system. In the absence of coupling to the heat bath, the system would remain in a single energy shell (the microcanonical ensemble) and if integrable, all the trajectories would be regular. When this system is coupled to the thermostat, the energy is no longer conserved as the system is driven from one energy shell to another. The faster the driving rate, the faster the system thermalises. In the case of a nonlinear system, the system is chaotic even on a given energy shell, and such systems respond more readily to the application of the thermostat (see Fig. 1).

Although the thermostat function does not depend on the precise value of the parameter Q, it is well known that it is important to choose this parameter carefully for most practical purposes. We examined the variation of the beat frequency as a function of Q, and these results are shown in Fig. 2. For $\alpha = 0$, the beat frequency is proportional to $1/Q$ and for low values of α the behaviour of thesystem does not change significantly. But when nonlinearity is high, there is marked deviation for high Q, whereas the integrable system shows regular dynamics even after being coupled to the thermostat [9] and thus does not thermalise; the present system thermalises even in this regime of Q.

3. Lyapunov exponents

The extent of chaos in a dynamic system is best quantified through the Lyapunov exponents [10,11],

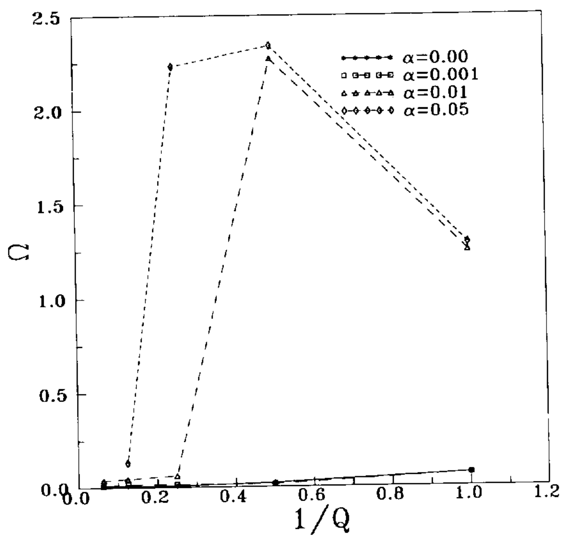

Fig. 2. Variation of the beat frequency, Ω, as a function of the heat-bath inverse mass parameter, Q, for different values of α.

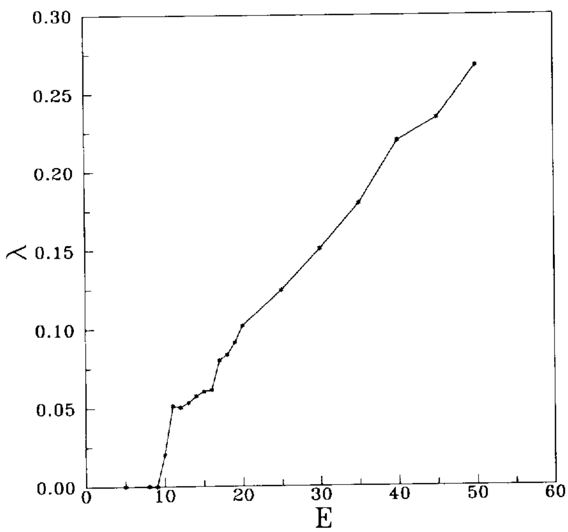

Fig. 3. Plot of the maximal Lyapunov exponent, λ, as a function of the system energy, E. The value of the perturbation parameter α was taken as 0.05.

which measure the rate of divergence of trajectories in the phase space. The process of thermalisation, since it is related to the ergodicity of the extended system can also be studied through the behaviour of the largest Lyapunov exponent. (For a hamiltonian dynamic system with N degrees of freedom and M conserved quantities, there are $2N$ Lyapunov exponents of which $2M$ are strictly zero [14]. Furthermore, they come in pairs of positive and negative exponents so that the sum of all the Lyapunov exponents is zero. The largest of these measures the local rate of divergence of trajectories, and thus aids in quantifying the chaotic behaviour).

The maximal Lyapunov exponent (MLE), λ, can be calculated as [15]

$$\lambda = \lim_{t\to\infty} \frac{1}{t} \lim_{\Delta x_0 \to 0} \left(\log \frac{\Delta\vec{x}}{\Delta\vec{x}_0} \right) \tag{16}$$

where $\Delta\vec{x}_0$ is the difference in the initial conditions of the two trajectories and $\Delta\vec{x}$ is the difference at time t. To evaluate λ along the trajectory, $\Delta\vec{x}$ is propagated in time and follows the equation of motion

$$\dot{\Delta\vec{x}} = J\Delta\vec{x} \tag{17}$$

where J is the Jacobian. An extension of the above

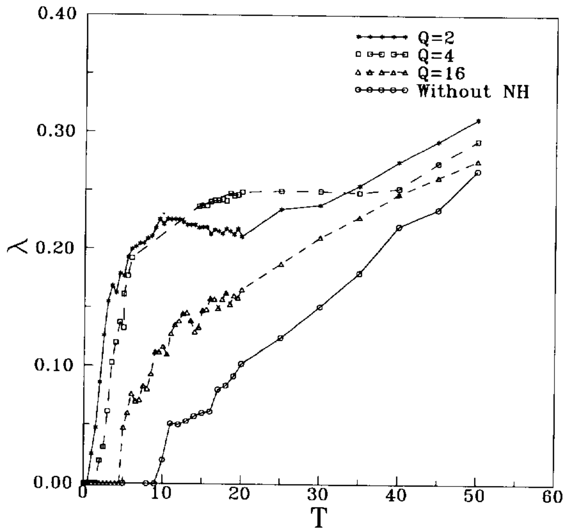

Fig. 4. Variation of λ with respect to temperature T for different values of the parameter Q. The value of the perturbation parameter is $\alpha = 0.05$. The curve labelled "without NH" is for the isolated system (without thermostat).

algorithm can be used to compute all the exponents [16]; here, however, we focus on the MLE. The Jacobian for the isolated system is

$$J = \begin{pmatrix} 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \\ -1 - 2\alpha q_2^2 & -4\alpha q_1 q_2 & 0 & 0 \\ -4\alpha q_1 q_2 & -1 - 2\alpha q_1^2 & 0 & 0 \end{pmatrix} \qquad (18)$$

The MLE was evaluated as a function of total energy, and the results are shown in Fig. 3, for $\alpha = 0.05$. There is an apparently abrupt transition to chaos at an energy of around $E \approx 9$, which is typical behaviour for perturbed oscillator systems. Beyond this "critical" energy, there is essentially a monotonic increase in the MLE.

The Jacobian of the extended system (we omit the equations for s) is

Shown in Fig. 4 is a plot of the MLE versus temperature for typical values of Q. In all cases, the MLE of the thermostat is enhanced above the value of the exponent in the isolated system, although the overall dependence on the temperature is very similar to that of the MLE on the total energy. Some correspondence between the canonical and microcanonical results can be made by noting that at temperature T, the most probable energy is $\bar{E} = k_B T$. These microcanonical results are also superimposed in Fig. 4, and one can clearly see that the extended system is effectively more chaotic than the isolated system. This result is not entirely unexpected, but it is also gratifying to note that for both high and low Q values, unlike the case of the isotropic oscillator, the onset of ergodicity is earlier for the extended system, with the high Q limit following the curve of the isolated system more closely. However, fluctuations in the value of the MLE are higher in the former case, specially in the intermediate temperature regime. This is due to the competition between the temperature T and the parameter Q. Raising the temperature, T has the effect of making the system more ergodic, while decreasing the value of Q makes the system more thermalised.

4. Discussion and summary

In this paper we have studied the effect of the Nosé thermostat on a nonlinear, nonintegrable dynamic system with two degrees of freedom. The effect of the thermostat on *any* system is to accelerate ergodic behaviour by driving the system from one energy shell to another, with the speed of thermalisation depending (inversely) on the parameter Q. Although the Nosé–Hoover equations are now routinely used in a variety of applications,

$$J = \begin{pmatrix} 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 \\ -1 - 2\alpha q_2^2 & -4\alpha q_1 q_2 & -\zeta & 0 & -p_1 \\ -4\alpha q_1 q_2 & -1 - 2\alpha q_1^2 & 0 & -\zeta & -p_2 \\ 0 & 0 & 2p_1/Q & 2p_2/Q & 0 \end{pmatrix} \qquad (19)$$

the reliability of such a procedure can only be assessed by studying the detailed dynamics of systems with few degrees of freedom. We find that thermalisation proceeds more rapidly in the presence of nonintegrable terms in the hamiltonian, when the isolated system is itself capable of chaotic behaviour; this enhances ergodicity in the extended system. (Although this behaviour is guaranteed for all Q, we also note that intermediate values are, for practical reasons, optimal).

Confirmation of this is provided by studying the variation of the largest Lyapunov exponent, which is significantly larger in the extended system than in the isolated system at comparable energies. The thermostatted system effectively wanders between different energy shells, with the time spent in each shell determined by the canonical distribution. (Such behaviour is reminiscent of mechanisms that enhance mixing in chaotic flows, as proposed by Ottino [17]).

Our present results complement those of Nosé [9] who observed that even for the integrable case of multidimensional oscillators, the absence of low order commensurability in the frequencies was sufficient to give ergodic behaviour in the extended system. We have shown here that addition of nonintegrable terms has the same effect, and provides ergodicity, even when the frequencies remain commensurable.

Acknowledgements

This work has been supported in part by the Department of Science and Technology, India, under Grant No. SP/S2/MO5/92, and by the CSIR, India.

References

[1] M.P. Allen and D.J. Tildesley, Computer Simulation of Liquids, Oxford University Press, Oxford, 1987.
[2] S. Nosé, Mol. Phys., 52 (1984) 255; J. Chem. Phys., 81 (1984) 511; W.G. Hoover, Phys. Rev. A, 31 (1985) 1695.
[3] I. Hamilton, Phys. Rev. A, 42 (1990) 7467.
[4] H.A. Posch, W.G. Hoover and F.J. Vesely, Phys. Rev. A, 33 (1986) 4233.
[5] A. Bulgac and D. Kusnezov, Phys. Rev. A, 42 (1990) 5045.
[6] S. Nosé and F. Yonezawa, J. Chem. Phys., 84 (1986) 1803.
[7] R. Car and M. Parrinello, Phys. Rev. Lett., 55 (1985) 2471.
[8] H.L. Davis, J. Jellinek and R.S. Berry, J. Chem. Phys., 86 (1987) 6456; See, e.g. S. Sugano, Microcluster Physics, Springer, Berlin, 1991 for applications in cluster physics.
[9] S. Nosé, Phys. Rev. E, 47 (1993) 164.
[10] A.J. Lichtenberg and M.A. Lieberman, Regular and Stochastic Motion, Springer, Berlin, 1983.
[11] M. Tabor, Chaos and Integrability in Dynamical Systems, Wiley, New York, 1986.
[12] M. Hénon and C. Heiles, Astron. J., 69 (1964) 73.
[13] R.A. Pullen and A.R. Edmonds, J. Phys. A, 14 (1981) L477.
[14] H.D. Meyer, J. Chem. Phys., 84 (1986) 3147.
[15] G. Benettin, L. Galgani and J.M. Strelcyn, Phys. Rev. A, 14 (1976) 2338.
[16] T.S. Parker and L.O. Chua, Practical Numerical Algorithms for Chaotic Systems, Springer, New York, 1989.
[17] J.M. Ottino, The Kinematics of Mixing, Stretching, Chaos and Transport, Cambridge University Press, Cambridge, 1989; see also, N. Gupte, in Computational Aspects in Chaos and Nonlinear Dynamics, G. Ambika and V.M. Nandakumaran (Eds.), Wiley Eastern, New Delhi, 1994, p. 48.