Statistical mechanics of Fermi-Pasta-Ulam chains with the canonical ensemble

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Low-energy vibrations of a Fermi-Pasta-Ulam-β (FPU-β) chain with 16 repeat units are analyzed with the aid of numerical experiments and the statistical mechanics equations of the canonical ensemble. Constant temperature numerical integrations are performed by employing the cubic coupling scheme of Kusnezov *et al.* [Ann. Phys. **204**, 155 (1990)]. Very good agreement is obtained between numerical results and theoretical predictions for the probability distributions of the generalized coordinates and momenta both of the chain and of the thermal bath. It is also shown that the average energy of the chain scales linearly with the bath temperature. [S1063-651X(97)06603-8]

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Thermodynamics constitutes functions of the state, and statistical mechanics establishes the bridge between the distribution functions and the functions of the state. Until the paradigm shift in 1955 created by Fermi, Pasta, and Ulam (FPU) [1], these working definitions had been thought to be valid only in the case of a mechanical system containing very large number of degrees of freedom (DOF) for which ergodicity is very likely satisfied. The *raison d'être* of the so-called FPU analysis was to test the ergodicity for a system with a considerably smaller number of DOF. This analysis necessitates numerical experiments. These ''experiments'' are basically numerical integrations of the equations of motion of the system under consideration. The mechanical system used in the original FPU study is a one-dimensional chain consisting of 64 repeat units (masses). The historical perspective of the developments since then may be found in an excellent review by Ford [2], with his personal reflections. For the mechanical systems with relatively small DOF, consensus has been established in that there exists a threshold energy for each mechanical system above which the system satisfies equipartition. Inasmuch as the system equilibrates, the laws of statistical mechanics and thermodynamics may be utilized.

Some modifications in the equations of statistical mechanics are necessary when we deal with small systems. Hill [3] was the one who generalized the differential equations of macroscopic thermodynamics so as to consider small (microscopic) systems. Berdichevsky and his collaborators [4–6] have taken a different path, along which they have studied Henon-Heiles [5] and FPU problems [6] both numerically and theoretically. Theoretical formulations are based on the work of Berdichevky [4]. In this work, the author showed that the laws of statistical mechanics based upon the microcanonical ensemble must be slightly modified for small systems. In the applications, ergodicity was checked with the aid of numerical simulations [5,6]. And it has been shown that numerical and theoretical probability distribution functions are in very good agreement when ergodicity is achieved during the numerical studies.

Numerical experiments performed on FPU systems to date may be viewed as microcanonical formulations. In this study, we consider canonical dynamics formulations [7–19]. Andersen [7] proposed that the interaction with a thermal bath may be simulated by stochastization of the system. This may be achieved by the Brownian dynamics (BD) technique which guarantees an approach to equilibrium. The BD technique includes a phenomenological dissipation coefficient and a Gaussian white-noise forcing term, two of which are related via fluctuation-dissipation theorem. With these two ingredients, BD simulations takes account of the interaction with a thermal bath, which resembles infinite degrees of freedom.

Nosé [8], in his pioneering work, demonstrated that the interaction of a finite-dimensional system with a thermal bath can be simulated by simply adding a single degree of freedom to the original system. The new system which consists of the original system and an additional degree of freedom is referred to as an extended system. It is possible to show that canonical ensemble of the original system is equivalent to the microcanonical ensemble of the extended system, provided that dynamics of the extended system is ergodic on the constant energy surface. The main difficulty in Nosé's scheme was the predictability of ergodicity as put forward by Hoover [9], who also derived a computationally amenable form of the Nosé equation. Hoover and his collaborators [10] demonstrated the inadequate thermalization when they applied the Nosé-Hoover equation to the one-dimensional harmonic oscillator. Later, Cho and Joannopoulos [11] showed that a Lennard-Jones potential system can be ergodic, but on very large time scales. It should also be noted that one cannot modify the couplings of the system to the temperature bath in Nosé's scheme.

Kusnezov *et al.* [12] introduced another scheme which is called a cubic coupling scheme and activates the coupling to the thermal bath with two additional degrees of freedom. The authors also demonstrated that their scheme suffices to achieve ergodicity of the extended system. The main difference between the studies of Nosé [8] and Kusnezov *et al.* [12] is that the former is a Hamiltonian dynamics, which is ergodic in the subspace, while the latter is canonical dynamics, which is non-Hamiltonian and ergodic in the extended space.

In this work, we follow the work of Kusnezov *et al.* [12] and perform canonical numerical experiments on a FPU-β chain. We compare the results from simulations with the theoretical calculations from the statistical mechanics formu-

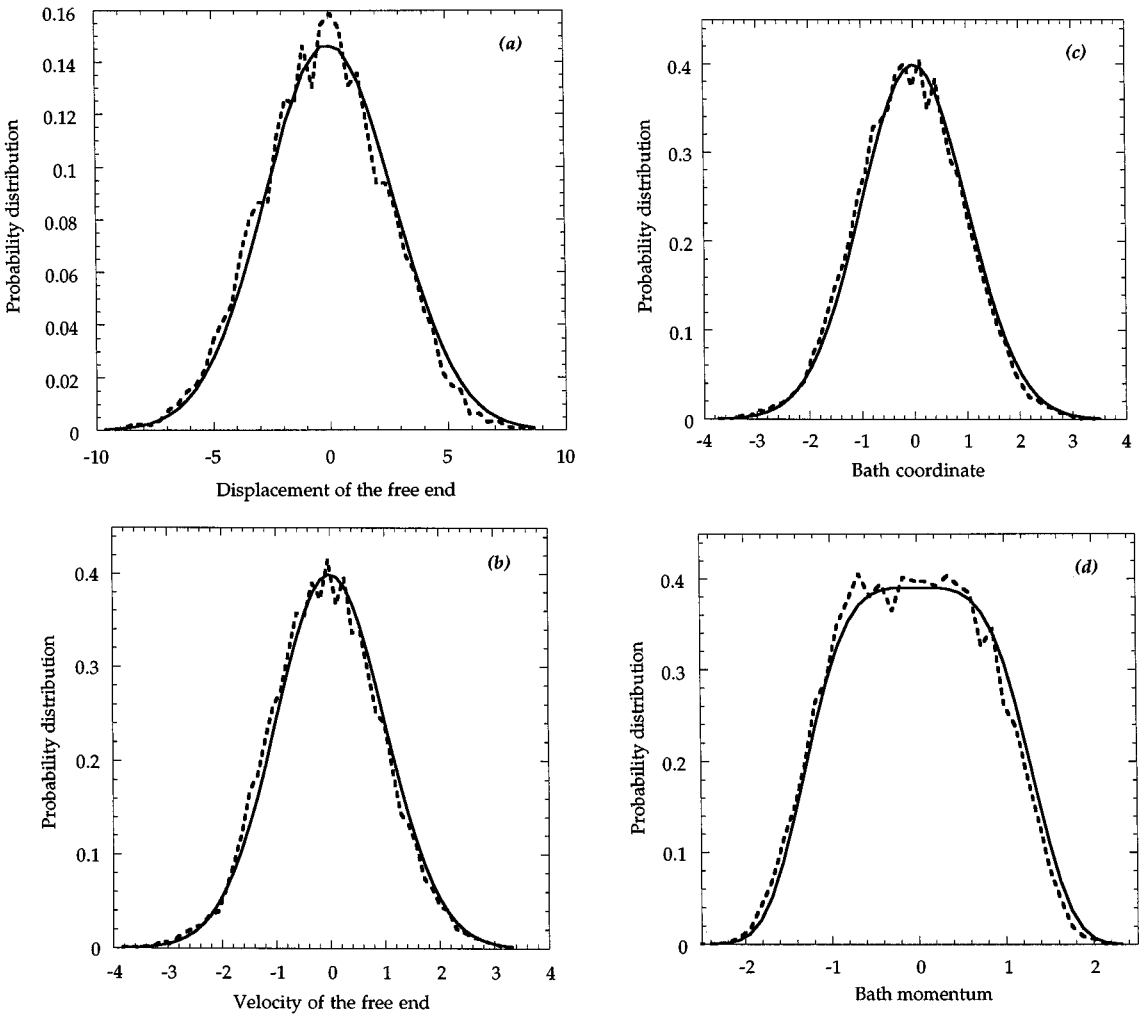

FIG. 1. Normalized probability distributions of the (a) displacement of the free end (q_{16}), (b) velocity of the free end (p_{16}), (c) thermal bath coordinate (ζ), and (d) thermal bath momentum (ξ). Solid lines denote the theoretical predictions [Eqs. (3) and (4)] and dashed lines are obtained from numerical experiments.

lations of the canonical ensemble. It is found that the theoretical and numerical probability distributions are in very good agreement and the average energy of the FPU chain varies linearly with the bath temperature.

A one-dimensional chain containing N number of repeat units is considered. Adjacent repeat units communicate with each other via an interaction potential. The interaction potential consists of quadratic and quartic functions of the difference between the generalized coordinates of the consecutive units. This model is usually referred to as the FPU-β model. Its total energy (Hamiltonian) may be written as

$$E(q,p)=\sum_{i=1}^{N}\frac{1}{2}p_i^2+\sum_{i=1}^{N}\frac{1}{2}(q_i-q_{i-1})^2+\frac{1}{4}(q_i-q_{i-1})^4, \tag{1}$$

where q_i and p_i are the generalized coordinate and the momentum of the ith repeat unit. We take $q_0=0$. The first sum in this equation is the kinetic energy and the second sum is the potential energy of interactions, which can be symbolically shown as $U(q)$.

Constant DOF, volume, and energy (N,V,E) ensemble (microcanonical ensemble) integration of the FPU-β system has been performed successfully and compared with the finite DOF thermodynamics by Berdichevsky and his collaborators [6]. It was shown that as the number of DOF increases ($N\geqslant 32$) the relative error in probability distributions between the numerical results and the theoretical estimates becomes less pronounced due to accurate achievement of ergodicity. Nevertheless, for a smaller number of DOF, the error grows exponentially. This makes the use of the (N,V,E) ensemble inappropriate for theoretical calculations on small systems.

For the FPU-β chains containing a number of repeat units less than 32, constant DOF, volume, and temperature (N,V,T) ensemble (canonical ensemble) may be utilized for theoretical estimations. However, another computational scheme is then necessary for constant temperature numerical integrations of the equations of motion. Here we utilize the cubic coupling scheme of Kusnezov *et al.* [12]. According to this scheme, the following extended system needs to be integrated:

$$\dot{q}_i=p_i-\xi q_i^3,$$

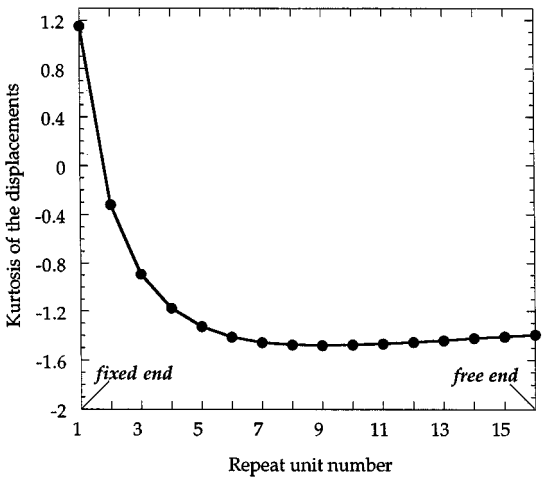

FIG. 2. Kurtosis of the displacements for each repeat unit calculated using Eq. (5). It is realized that the probability distribution becomes flatter as a repeat unit departs from the fixed end, and stays at the same flatness after the first half of the chain.

$$\dot{p}_i = -\frac{\partial U}{\partial q_i} - \zeta^3 p_i,$$

$$\dot{\zeta} = \alpha\left(\sum_{i=1}^{N} p_i^2 - NT\right),$$

$$\dot{\xi} = \gamma\left(\sum_{i=1}^{N} q_i^3 \frac{\partial U}{\partial q_i} - 3T\sum_{i=1}^{N} q_i^2\right), \tag{2}$$

where ζ and ξ represent the infinite DOF that bath constitutes. Here ζ and ξ may be referred to as the bath coordinate and the bath momentum, respectively. In Eq. (2), T is the bath temperature, and α and γ are free parameters that may be taken as $1/T$ and $1/T^2$, respectively [12]. Kusnezov and his collaborators [13–15] have made further comments on the best choices of free parameters in different physical models. The thermal unnormalized probability distributions that follow from this scheme are

$$f(p_i) = e^{-p_i^2/2T}, \quad f(\zeta) = e^{-\zeta^2/2T\alpha},$$

$$f(q_1,\ldots,q_N) = e^{-U(q)/T}, \quad f(\xi) = e^{-\xi^4/4T\gamma}. \tag{3}$$

These theoretical distributions are compared with those resulting from the numerical integrations of Eq. (2).

A FPU-β chain with 16 repeat units is considered. One end of the chain is fixed, the other is free. Initial conditions with different energies are assigned. The initial energy given to the chain is well below the threshold energy of the system. Thus, the FPU-β system cannot satisfy equipartition with this energy level. However, in the (N,V,T) formulation, regardless of the value for the excitation energy, the average energy of the chain converges to a constant value. This makes it possible to study the low-energy vibrations (lower than the threshold value) of the FPU chains. Equations of the motion in the extended system, consisting of the FPU-β chain and the bath [Eqs. (2)] are integrated numerically by the Bulirsch-Stoer method [20]. This method conserves the energy at each time step; therefore, the (N,V,E) integration of the extended system is accomplished successfully.

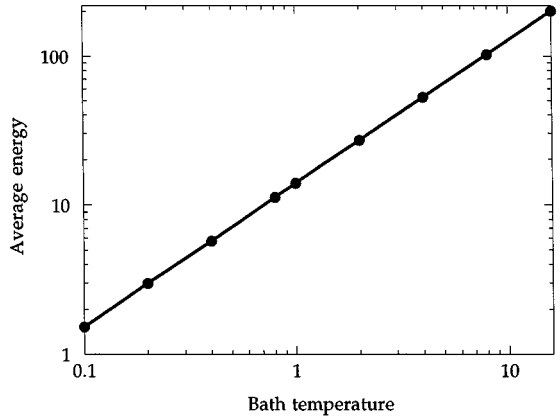

FIG. 3. Average energy of the chain with respect to the thermal bath temperature. Solid circles represent the points obtained numerically. The solid line is to guide the eye.

The normalized probability distributions of the free end coordinate, q_{16}, and the free end momentum, p_{16}, are shown in Figs. 1(a) and 1(b), respectively. The normalized probability distributions of the bath coordinate, ζ, and the bath momentum, ξ are shown in Figs. 1(c) and 1(d), respectively. Dashed lines are used for the results obtained from numerical integrations by using 10^4 data points. Solid lines, on the other hand, are calculated using theoretical results [Eqs. (3)]. The probability distribution of the jth generalized coordinate is calculated using the following integral:

$$f(q_j) = \int_{-\infty}^{\infty} e^{-U(q_1,\ldots,q_N)/T} dq_1 dq_2 \cdots dq_{j-1} dq_{j+1} \cdots dq_N. \tag{4}$$

In order to perform the integration, the transformation $\epsilon_j = q_j - q_{j-1}$ is used. For the linear case, after applying the saddle-point approximation, the result is simply $f(q_j) = \mathcal{C} e^{-q_i^2/2jT}$. For the general case, however, the closed form solution cannot be obtained due to the inability of evaluating the integral $\int_{-\infty}^{\infty} e^{-[(1/4)\epsilon^4 + (1/2)\epsilon^2]/T - a\epsilon} d\epsilon$ ($a>0$ is a constant) in closed form. This integral is also evaluated numerically. Very good agreement between the theoretical and numerical results is observed. It is common in all curves in Fig. 1 that the fluctuations in the numerical results are amplified around the maximum point of the probability distributions of the generalized coordinates and momenta. Longer simulation periods would definitely smoothen the fluctuations.

In Fig. 2, Kurtosis of the displacements for each repeat unit along the chain is shown. The definition of the Kurtosis for the jth unit is

$$K(q_j) = \left[\frac{1}{\mathcal{N}}\sum_{i=1}^{\mathcal{N}} \left(\frac{q_j^{(i)} - \overline{q_j}}{\sigma_j}\right)^4\right] - 3, \tag{5}$$

where $q_j^{(i)}$ stands for the generalized coordinate of the jth unit at the ith time step, and $\mathcal{N}$ is the number of time steps. Here, $\overline{q_j}$ is the mean and σ_j is the standard deviation of the

values $q_j^{(1)}, q_j^{(2)}, \ldots, q_j^{(\mathcal{N})}$. Kurtosis quantifies the relative peakedness or flatness of a distribution. Herein the -3 term makes the Kurtosis zero for a normal distribution. Positive and negative Kurtosis represent the character of the distribution with respect to peakedness and flatness, respectively. It is recognized that the probability distribution becomes shallower immediately after the fixed end. And it converges to a limiting distribution after the seventh unit from the fixed end with an almost constant value -1.42.

We observe that the average energy of the FPU-β chain—irrespective of its initial value—converges to a constant value $\langle E \rangle$. In Fig. 3, the average energy is shown to be linearly proportional to the bath temperature. Solid circles designate the results from numerical experiments; the solid line is to guide the eye. log-log axes are employed so as to show clearly the numerical results for both lower and higher ends of the temperature spectrum.

Two main conclusions can be drawn from this study: (1) probability distributions for the generalized coordinates and momenta of FPU chains can be evaluated accurately with the aid of statistical mechanics laws. Those chains may consist of small number of repeat units, and energy levels for the initial excitation can be lower than the threshold energy; (2) the average energy of the FPU chain studied converges to a constant value independent of its initial value, and it changes linearly with the bath temperature for all ranges of the temperature spectrum.

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[1] E. Fermi, J. Pasta, S. Ulam, and M. Tsingou, Los Alamos Report No. LA-1940, 1955 (unpublished).
[2] J. Ford, Phys. Rep. **213**, 271 (1992).
[3] T. L. Hill, J. Chem. Phys. **36**, 153 (1962).
[4] V. L. Berdichevsky, J. Appl. Math. Mech. **52**, 738 (1988).
[5] V. L. Berdichevsky and M. von Alberti, Phys. Rev. A **44**, 858 (1991).
[6] E. H. Mueller, M. S. thesis, Georgia Institute of Technology, School of Aerospace Engineering, 1994 (unpublished).
[7] H. C. Andersen, J. Chem. Phys. **72**, 2384 (1980).
[8] S. Nosé, J. Chem. Phys. **81**, 511 (1984).
[9] W. G. Hoover, Phys. Rev. A **31**, 1695 (1985).
[10] H. A. Posch, W. G. Hoover, and F. J. Veseley, Phys. Rev. A **33**, 4253 (1986).
[11] K. Cho and J. D. Joannopoulos, Phys. Rev. A **45**, 7089 (1992).
[12] D. Kusnezov, A. Bulgac, and W. Bauer, Ann. Phys. (NY) **204**, 155 (1990).
[13] D. Kusnezov, Phys. Lett. B **289**, 395 (1992).
[14] D. Kusnezov, A. Bulgac, and J. Sloan, Nucl. Phys. **A545**, 537c (1992).
[15] D. Kusnezov and J. Sloan, Nucl. Phys. **B409**, 635 (1993).
[16] S. Nosé, Phys. Rev. E **47**, 164 (1993).
[17] K. Cho, J. D. Joannopoulos, and L. Kleinman, Phys. Rev. E **47**, 3145 (1993).
[18] W. G. Hoover, Phys. Lett. A **204**, 133 (1995).
[19] W. G. Hoover and B. L. Holian, Phys. Lett. A **211**, 253 (1996).
[20] W. H. Press, S. A. Teukolsky, W. T. Vetterling, and B. P. Flannery, *Numerical Recipes* (Cambridge University Press, Cambridge, England, 1992).