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LETTER TO THE EDITOR

Energetic motion of end-particles in constrained dynamical systems

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Abstract.

We propose a planar chain system, which is a simple mechanical system with a constraint. It is composed of N masses connected by $N - 1$ light links. It can be considered as a model of a chain system, e.g., a polymer, in which each bond is replaced by a rigid link. The long time average of the kinetic energies of the masses in this model is numerically computed. It is found that the average kinetic energies of the masses are different and masses near the ends of the chain have large energies. We derive an approximate expression for the average kinetic energy, which is in qualitative agreement with the numerical results.

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Figure 1. A planar chain system

Information on energy distribution in many-body systems is quite important for both theoretical and practical purposes. If a system is in thermal equilibrium, then, according to the principle of equipartition of energy, the average kinetic energy is equally distributed among all the degrees of freedom. In systems with constraints, it is known that the principle of equipartition is realized in somewhat complicated way. It is not the usual kinetic energy of particles which have equal value [1, 2, 3, 4]. As a result, the average kinetic energies of the particles take different values. However, little attention is paid to how the average kinetic energies vary among particles.

In this letter, we introduce a system called a “planar chain system”, which is a simplified model of a chain system e.g., a polymer. The system have constraints that the distances between neighboring particles are fixed. We show that the average kinetic energy in this system is nonuniformly distributed in thermal equilibrium, and particles near the ends of the chain have larger kinetic energies. We explain the reason for the nonuniform distribution of energy. The energetic motion of end particles could provide a new insight into the behavior of chain systems.

Let us introduce the planar chain system. The planar chain system is composed of N particles (masses) connected by $N - 1$ links. The masses can rotate smoothly, as shown in Fig.1. The links are massless and have fixed lengths. The system is defined by the following Lagrangian L and constraints g_i ($i = 1, 2, \dots, N - 1$):

$$L = \sum_{i=1}^N \frac{m_i}{2} (\dot{x}_i^2 + \dot{y}_i^2) - U(\{\vec{r}_i\}) , \quad (1)$$

$$g_i(\{\vec{r}_j\}) \equiv \frac{1}{2} \{ |\vec{r}_{i+1} - \vec{r}_i|^2 - \ell_i^2 \} = 0, \quad (2)$$

where N is the number of particles, m_i is the mass of i 'th particle, $\vec{r}_i \equiv (x_i, y_i)$ represents the position of the i 'th particle, and ℓ_i is the length of the i 'th link. U represents potential energy. We consider (i) a free chain with $U \equiv 0$ and (ii) external potential $U \equiv \sum_{i=1}^N V(\vec{r}_i)$.

If we define φ_i as the angle between the i 'th link and the $-y$ direction (Fig.1), we can rewrite the Lagrangian without the constraints. First we consider the following relations: $x_{i+1} - x_i = \ell_i \sin \varphi_i$, $y_{i+1} - y_i = -\ell_i \cos \varphi_i$. Using the total mass M and the center of mass (X_G, Y_G) defined as $M \equiv \sum_{i=1}^N m_i$, $X_G \equiv \sum_{i=1}^N \frac{m_i}{M} x_i$, $Y_G \equiv \sum_{i=1}^N \frac{m_i}{M} y_i$, we obtain

$$x_i = X_G + \sum_{j=1}^{N-1} a_{ij} \sin \varphi_j, \quad y_i = Y_G - \sum_{j=1}^{N-1} a_{ij} \cos \varphi_j, \quad (3)$$

where a_{ij} is defined as

$$a_{ij} \equiv \begin{cases} \mu_j^< \ell_j & : j < i, \\ -\mu_j^> \ell_j & : j \geq i, \end{cases} \quad (4)$$

and

$$\mu_k \equiv \frac{m_k}{M}, \quad \mu_n^< \equiv \sum_{k=1}^n \mu_k, \quad \mu_n^> \equiv \sum_{k=n+1}^N \mu_k. \quad (5)$$

By a straightforward calculation, we obtain the Lagrangian (1) in terms of φ_i 's and (X_G, Y_G) as

$$L = \frac{M}{2}(\dot{X}_G^2 + \dot{Y}_G^2) + \frac{M}{2} \sum_{j,k=1}^{N-1} A_{jk}(\varphi) \dot{\varphi}_j \dot{\varphi}_k - U(X_G, Y_G, \{\varphi_i\}) \quad (6)$$

where

$$A_{jk}(\varphi) \equiv \mu_{\min(j,k)}^< \mu_{\max(j,k)}^> \cos(\varphi_{jk}) \ell_j \ell_k, \quad (7)$$

and $\varphi_{jk} \equiv \varphi_j - \varphi_k$.

We can consider this system as a simplified prototype of various chain systems, e.g., proteins, polymers and spacecraft manipulators, under the assumption that the frequencies of bond-stretching vibrations are quite high.

Now, we describe a method for numerical simulation. The Lagrangian that is expressed in terms of angles (6) is complicated and it is difficult to numerically integrate the equation of motion, in particular for large N . Hence, we use the original form of the Lagrangian (1) and the constraint g_i (2). Then, the equation of motion includes terms of the constraint, which are called ‘‘Lagrange multipliers’’ [5]. We determine Lagrange multipliers numerically at each integration step so that the constraint is satisfied [6]. Methods of this type, e.g., ‘‘SHAKE’’ and ‘‘RATTLE’’ algorithms, are widely used for molecular simulation in chemistry [7, 8, 9]. In addition, some of the algorithms are known to be symplectic [6]. Here, we use the forth-order symplectic integrator that is the composition of three successive second-order RATTLE algorithm [6]. In some cases, we verify the results by using an implicit Runge-Kutta method.

If $U \equiv 0$, the total angular momentum is conserved, hence, in this case, the energy distribution is different from the microcanonical distribution. In actual computations, we place the system in a potential wall composed of arcs of radius a : $U \equiv \sum_{i=1}^N V(\vec{r}_i)$, $V(\vec{r}) = 0.01 \sum_{j=1}^{N_{wall}} \left| |\vec{r} - \vec{R}_j| - a \right|^{-6}$. Then, the system exhibits strongly chaotic

Figure 2. Planar chain in potential wall. $N = 5$, $N_{wall} = 4$, $a = 4N\ell$, $R_j = (R, 0), (-R, 0), (0, R), (0, -R)$, $R = N\ell + \sqrt{a^2 - N^2\ell^2}$. $\ell_1 = \dots = \ell_{N-1} \equiv \ell$.

motion similar to billiards [10] and does not have any conserved quantities other than the total energy, hence the microcanonical distribution is restored.

Although the planar chain system is a simple system, its dynamics is complex; further, energy exchanges occur between various parts of the system. Fig. 3 shows a power spectrum of $x_1(t)$ with the external potential mentioned above. It is a broad continuous spectrum, which is a manifestation of chaotic motion [11].

Figure 3. Power spectrum of $x_1(t)$ for $0 \leq t \leq 32767$. $N = 5$. External potential in Fig.2 is used to obtain the spectrum.

Using the method described above, we compute the long time average of kinetic energy. If the averaging time is sufficiently large, the long time average and thermal

average can be assumed to be the same.

The kinetic energy of i 'th particle is defined as $K_i(t) \equiv \frac{m_i}{2} (\dot{x}_i^2 + \dot{y}_i^2)$, and its long time average is defined as

$$\overline{K_i} \equiv \frac{1}{t_{max}} \int_0^{t_{max}} K_i(t) dt, \quad t_{max} \rightarrow \infty. \quad (8)$$

Figure 4. Long time average of kinetic energy $\overline{K_i}$ vs. i (8). $N = 16$. $m_i = 1.0$ for all i and $\ell_i = 1.0$ for all i . The initial condition is as follows: $x_i = (i - 1) - N/2$, $y_i = 0$, $p_i^{(x)} = 0$ for all i , $p_1^{(y)} = -0.1$, and $p_i^{(y)} = 0.1 (i > 1)$. Here, $p_i^{(x)}$ and $p_i^{(y)}$ represent the x and y components of the momentum of the i 'th particle, respectively. The time step for integration is $dt = 0.001$. t_{max} (8) is 10^5 . The relative error for total energy (square root of the time average of the squared displacement) is $\sqrt{\Delta E^2/E_0^2} = 6.1 \times 10^{-11}$.

Figure 5. Convergence of kinetic energy K_i (8) in Fig.4 as a function of t_{max} .

Fig.4 shows a plot of the average kinetic energy of each mass $\overline{K_i}$ (8) against i for $N = 16$ planar chain system. We find that masses that are near the ends of the chain have large kinetic energies. We obtain this result for all the computed system sizes ($N \leq 128$). Fig. 5 shows the convergence of $\frac{1}{t_{max}} \int_0^{t_{max}} K_i(t') dt'$ as a function of t_{max} . The values shown in Fig.4 are well converged.

In order to understand this result let us recall the principle of equipartition of energy. The principle of equipartition of energy is stated as follows [2, 3, 4]: Suppose we have a system defined by a Hamiltonian

$$H(q, p) \equiv K(q, p) + V(q), \quad K(q, p) \equiv \sum_{i,j=1}^{\mathcal{N}} \frac{1}{2} \alpha_{ij}(q) p_i p_j, \quad (9)$$

where p_i and q_i are canonically conjugate to each other and $\mathcal{N}$ is the total number of degrees of freedom. If it is in thermal equilibrium at temperature T , then the following relation holds:

$$\left\langle \frac{1}{2} p_i \frac{\partial K}{\partial p_i} \right\rangle = \frac{1}{2} k_B T \quad (10)$$

(Summation over the index i is not taken in the left hand side.). The symbol $\langle \dots \rangle$ represents thermal average at T , and is defined as

$$\langle f(q, p) \rangle \equiv \frac{1}{Z} \int f(q, p) e^{-\beta H} d\Gamma, \quad (11)$$

for any function $f(q, p)$. Here, $d\Gamma$ is a volume element of phase space, Z is a partition function, and $\beta \equiv 1/k_B T$.

Let us define the “canonical kinetic energy” $K_i^{(c)}$ and the “linear kinetic energy” K_i as

$$K_i^{(c)} \equiv \frac{1}{2} p_i \frac{\partial K}{\partial p_i}, \quad K_i \equiv \frac{1}{2} m_i v_i^2, \quad (12)$$

respectively. Here, equipartition of energy means that the average values of $K_i^{(c)}$'s are equal at thermal equilibrium.

For systems such as gas models or lattice models, $\alpha_{ij}(q) = m_i^{-1} \delta_{ij}$ and $K_i^{(c)} = K_i$: hence, the principle of equipartition (10) simply means that $\langle \frac{1}{2} m_i v_i^2 \rangle = \frac{1}{2} k_B T$.

In the case of a planar chain system, we obtain the canonical momentum p_i that is conjugate to φ_i as $p_i \equiv \frac{\partial L}{\partial \dot{\varphi}_i} = \sum_{k=1}^{N-1} A_{ik}(\varphi) \dot{\varphi}_k$, Hence

$$H = \sum_{i=1}^{N-1} p_i \dot{\varphi}_i - L = \frac{1}{2} \sum_{i,j=1}^{N-1} A^{-1}(\varphi) p_i p_j + U(\varphi) \quad (13)$$

and the kinetic energy K reads

$$K = \frac{1}{2} \sum_{i,j=1}^{N-1} A^{-1}(\varphi) p_i p_j. \quad (14)$$

The matrix A^{-1} corresponds to $\alpha(q)$ in eq.(9). It is also known as “metric tensor” in the literatures which study holonomic constraints in classical systems of mass points[12], and widely used e.g. in simulating polymer chains [13, 14]. Since the matrix $A^{-1} \equiv \alpha$

depends on the coordinates, it is possible that the canonical kinetic energy K_i^c , which obey equipartition, is different from the linear kinetic energy K_i .

We obtain the canonical kinetic energy $K_i^{(c)}$ as

$$K_i^{(c)} \equiv \frac{1}{2} p_i \frac{\partial K}{\partial p_i} = \frac{1}{2} \sum_{k=1}^{N-1} A_{ik}(\varphi) \dot{\varphi}_k \dot{\varphi}_i . \quad (15)$$

It should be noted that $K_i^{(c)}$ is defined by variables of every part of the system, whereas K_i is defined only by the i -th particle. In other words, canonical kinetic energy $K_i^{(c)}$ is extended, whereas linear kinetic energy K_i is localized.

Figure 6. Long time average of canonical kinetic energy $\overline{K_i^{(c)}}$ (15) vs i . This plot is obtained by using the same data as that in Fig.4.

In order to see if the principle of equipartition of energy is realized, we show in Fig. 6 the long time average of K_i^c (15) for the same time series as that in Fig. 4. It is clearly shown that $\overline{K_i^{(c)}}$'s take almost the same value for all i . That is, equipartition of energy is realized for the planar chain system.

Now let us derive the distribution of linear kinetic energy shown in Fig. 4 by analytical calculation. By a straightforward calculation, we obtain

$$\frac{\langle K_i \rangle}{k_B T} = \frac{m_i}{M} + \frac{m_i}{2k_B T} \sum_{j,k=1}^{N-1} a_{ij} a_{ik} \langle \cos(\varphi_{jk}) \dot{\varphi}_j \dot{\varphi}_k \rangle . \quad (16)$$

To evaluate the second term, we adopt the following approximations:

$$\langle \cos(\varphi_{jk}) \dot{\varphi}_j \dot{\varphi}_k \rangle = 0 \quad \text{for } j \neq k, \quad (A^{-1})_{jj} \sim \frac{1}{A_{jj}} = \frac{1}{M \mu_j^{\leq} \mu_j^{\geq} \ell_j^2} . \quad (17)$$

(The matrix A^{-1} is included in $\exp(-\beta H)$.) These approximations indicate that the rotation of each link is statistically independent. Then, we obtain

$$\frac{\langle K_i \rangle}{k_B T} = \frac{m_i}{M} \left\{ 1 + \frac{1}{2} \left[\sum_{j=1}^{i-1} \left(\frac{\mu_j^{\leq}}{\mu_j^{\geq}} \right) + \sum_{j=i}^{N-1} \left(\frac{\mu_j^{\geq}}{\mu_j^{\leq}} \right) \right] \right\} . \quad (18)$$

Details of the calculation will be shown elsewhere [15].

If all the masses are the same, i.e., $m_1 = m_2 = \dots = m_N \equiv m$, then we obtain

$$\frac{\langle K_i \rangle}{k_B T} = \frac{1}{N} \left\{ 1 + \frac{1}{2} \left[\sum_{j=1}^{i-1} \left(\frac{j}{N-j} \right) + \sum_{j=i}^{N-1} \left(\frac{N-j}{j} \right) \right] \right\}. \quad (19)$$

Using this expression, we have

$$\frac{1}{\frac{m}{M} \frac{k_B T}{2}} (\langle K_{i+1} \rangle - \langle K_i \rangle) = \frac{N(2i - N)}{i(N - i)}. \quad (20)$$

Therefore

$$\begin{cases} N - 2i > 0 \Leftrightarrow i < \frac{N}{2} & \Rightarrow \langle K_{i+1} \rangle < \langle K_i \rangle, \\ N - 2i < 0 \Leftrightarrow i > \frac{N}{2} & \Rightarrow \langle K_{i+1} \rangle > \langle K_i \rangle. \end{cases} \quad (21)$$

Hence we obtain the following:

$$\langle K_1 \rangle > \langle K_2 \rangle > \dots < \langle K_{N-1} \rangle < \langle K_N \rangle. \quad (22)$$

It is clear that $\langle K_i \rangle$ is large at the ends of the chain and small at the center of the chain: this result is in qualitative agreement with the result of the numerical computation shown in Fig.4.

In this letter we have numerically shown that the average kinetic energy of each particle $\overline{K_i} \equiv \frac{1}{2} m_i v_i^2$ is larger near both ends of the chain for planar chain system. The nonuniform distribution of the linear kinetic energy is qualitatively explained by analytical calculation. Although it is already known for long time that K_i does not obey the principle of equipartition of energy for systems with constraints [1, 2], it is the first result that shows systematic variation of K_i .

It is clear that there are other models which show similar behavior. These models are systems with constraints, where the expression of the kinetic energy includes coordinates. In fact, it has been found that the behavior of linear kinetic energy in a multiple pendulum system is similar to that in the planar chain system [16]; and we will report detailed analysis elsewhere [17]. In polymer science, the three-dimensional version of this model is known as a “freely jointed chain” [18, 19]. We expect that the behavior of the kinetic energy in the freely jointed chain will be similar to that in the planar chain system.

It should be noted how solvent affect the chain dynamics. The effect of solvent will act as a part of heat bath. In thermal equilibrium, the ends of the chain is still energetic even with the solvent.

This result would have important implications for the dynamics of chain systems such as molecules, proteins, polymers, and some artificial objects. For example, in polymer science, it is well known that atoms situated near the ends of the polymer chain have characteristic behavior called the “end effect” [20]. Energetic motion of end-particles we found in planar chain systems can be closely related to the origin of the end effect of polymers.

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