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Temperature, least action, and Lagrangian mechanics

William G. Hoover

Department of Applied Science, University of California at Davis / Livermore and Lawrence Livermore National Laboratory, Livermore, CA 94551-7808, USA

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Abstract

Temperature is considered from two different mechanical standpoints. The more general approach uses Hamilton's least action principle. From it we derive thermostating forces identical to those found using Gauss' Principle. This approach applies to equilibrium and nonequilibrium systems. The Lagrangian approach is different, and less useful, applying only at equilibrium.

Keywords: Least action principle; Nonequilibrium; Lagrangian mechanics

1. Introduction

Feynman repeatedly emphasized the generality of Hamilton's principle of least action [1], the physical law from which both kinds of mechanics, classical and quantum, follow. The principle states that the observed trajectory $\{q(t)\}$ is that which minimizes the action integral,

$$\delta \int L(q, \dot{q}, t) dt \equiv \delta \int (K - \Phi) dt \equiv 0,$$

where K is the kinetic energy, Φ is the potential energy, and $L(q, \dot{q}) \equiv K - \Phi$ is the Lagrangian. The integration time interval is fixed, as are also the coordinate sets at both end points. Here we restrict our attention to equilibrium or nonequilibrium many-body systems with kinetic energies quadratic in the velocities and potential energies which depend only on the coordinates $\{q\}$

$$K \equiv \sum m\dot{q}^2/2, \quad \Phi \equiv \Phi(q).$$

When the context is clear we use just a single q or \dot{q} to represent whole sets.

Lagrangian mechanics is particularly well-suited to the treatment of *constrained* systems. Constraints, used first to represent mechanical linkages and couplings, have more recently been used in molecular simulations, where they maintain the shape of a polyatomic molecule and reduce the number of dynamical equations to be integrated. The usual approach is to add a "Lagrange multiplier" to the Lagrangian in such a way as to impose the constraint without affecting energy conservation [2,3]. For instance, a particle with unit mass, constrained to circle the origin, at unit radius, can be described with the Lagrangian

$$L(x, y, \dot{x}, \dot{y}) = \frac{1}{2}(\dot{x}^2 + \dot{y}^2) + \lambda(r^2 - 1).$$

In this case, the Lagrangian equations of motion,

$$(d/dt)(\partial L/\partial \dot{q})_q = (\partial L/\partial q)_{\dot{q}},$$

give

$$\ddot{x} = 2\lambda x, \quad \ddot{y} = 2\lambda y.$$

The value of the Lagrange multiplier λ follows from the second derivative of the constraint

$$(d/dt)^2(r^2 - 1) = 2r \cdot \ddot{r} + 2\dot{r}^2 = 0 = 4\lambda r^2 + 2\dot{r}^2.$$

It is unnecessary to specify whether the Lagrange multiplier depends upon time, upon space, or even space, velocity, and time simultaneously, because the corresponding derivatives in the equations of motion would all be multiplied by the constraint $r^2 - 1$, and therefore vanish automatically.

In the next two sections we apply the two ideas just described, Hamilton's principle and Lagrangian constraints, to the more complicated case of constraining temperature(s) in many-body systems [3,4]. As is usual in classical nonequilibrium statistical mechanics, we define temperature [5] in terms of the mean-squared kinetic energy of a typical Cartesian degree of freedom,

$$kT \equiv \langle m\dot{x}^2 \rangle.$$

2. Temperature and Hamilton's principle

Let us apply the least action principle to trajectories defined in the infinitesimal time interval between $-dt$ and $+dt$, considering all the coordinates to be fixed at the endpoints, and with the set of coordinates at the central time, $\{q_0\}$, able to vary [6]. The centered-difference approximation to Hamilton's principle,

$$\delta \int L(q, \dot{q}) dt = 0,$$

is

$$\begin{aligned} \delta q_0 (\partial/\partial q_0) \left\{ (m/2 dt^2) [(q_0 - q_-)^2 + (q_+ - q_0)^2] \right. \\ \left. - \frac{1}{2} (\Phi_- + 2\Phi_0 + \Phi_+) \right\} dt \\ \equiv \delta q_0 [(m/dt^2)(2q_0 - q_- - q_+) + F_0] dt = 0, \end{aligned}$$

giving the usual Störmer–Verlet equation of motion [6,7]. To add temperature we introduce a Lagrange

multiplier ζ to insure that the solution is consistent with the variation of the isokinetic constraint,

$$\begin{aligned} \delta q_0 (\partial/\partial q_0) (m/2 dt^2) [(q_0 - q_-)^2 - (q_+ - q_0)^2] \\ = 0. \end{aligned}$$

Adding the two variational equations, and then taking the limit $dt \rightarrow 0$ gives the isokinetic differential equation of motion,

$$m\ddot{q} = F - \zeta m\dot{q}. \quad (1a)$$

The Lagrange multiplier ζ can be identified, as in the simple rigid-rotor example, by evaluating the time derivative of the constraint. The result for the Lagrange multiplier ζ (which in this case has the form of a "friction coefficient") is

$$\zeta \equiv \sum F \cdot \dot{q} / \sum m\dot{q}^2, \quad (1b)$$

and provides familiar time-reversible constraint forces. This result was already known to follow from Gauss' principle of least constraint [8,9], but Hamilton's least action principle is more general, because it promises also the possibility of extending the thermostat idea to nonequilibrium quantum systems. In the following section we will see that a straightforward application of classical Lagrangian mechanics to the same problem yields a less useful result.

3. Temperature and Lagrangian mechanics

If we choose to use a Lagrange multiplier, λ , which varies with time, and can also depend upon the coordinates and velocities, and use it to impose the constant-kinetic-energy constraint,

$$L = \sum \frac{1}{2} m\dot{q}^2 - \Phi(q) + \lambda(t) \left(\sum \frac{1}{2} m\dot{q}^2 - K_0 \right),$$

the resulting equation of motion is

$$\begin{aligned} (d/dt) [m\dot{q}(1 + \lambda)] &= F(q) \\ \Rightarrow m\ddot{q}(1 + \lambda) + \dot{\lambda}m\dot{q} &= F(q). \end{aligned}$$

Multiplying by \dot{q} , and summing over degrees of freedom, gives a simple differential equation for λ ,

$$\begin{aligned} \dot{\lambda} \sum m\dot{q}^2 = 2\dot{\lambda}K_0 = \sum F \cdot \dot{q} &\equiv -\dot{\Phi} \equiv -\dot{E} \\ \Rightarrow \lambda = (E_0 - E)/2K_0, \end{aligned}$$

where E_0 is the energy at the initial time, $t = 0$.

Notice that the *time derivative* of the Lagrange multiplier, $\dot{\lambda}$, is exactly equal to the friction coefficient ζ found previously using the principle of least action. To make this identification explicit, we write the present corresponding time-reversible Lagrangian equation of motion in terms of both these multipliers, $\zeta \equiv \dot{\lambda}$ and λ ,

$$m\ddot{q} = [F(q) - \zeta m\dot{q}] / (1 + \lambda),$$

$$\zeta \equiv \sum F \cdot \dot{q} / \sum 2K_v.$$

The equation of motion has an interesting form. For small fluctuations in the energy, as for instance occur in a large equilibrium system, the Lagrange multiplier λ is small, and the motion reduces to the Gaussian form (1) found above. On the other hand, in a nonequilibrium steady-state system, the integrated energy change (which is mainly heat extracted by the thermostating constraint forces), and the Lagrange multiplier λ , grow without bound, so that the equations have no long-time solution.

Thus the Lagrange-multiplier approach, unlike the principle of least action, is *not applicable* to nonequilibrium systems. This finding confirms Feynman's emphasis of the fundamental nature of least action. Evidently classical Lagrangian mechanics is restricted to equilibrium problems in a way which the principle of least action is not.

4. Summary

We have here generalized the basis of Gaussian isothermal mechanics by deriving the equations of motion directly from Hamilton's least action principle. This approach yields algorithms useful in simulating nonequilibrium systems too, by restricting the number of degrees of freedom to be constrained. For very recent summaries of nonequilibrium work see Refs. [10,11]. In the simple case of nonequilibrium many-body heat flow, a set of bulk particles obeys the usual Newton equations, while two reservoirs, one hot and one cold, obey the constrained Gauss equations of motion (1) with two separate friction

coefficients, $\{\zeta_T\}$. These same ideas apply to isobaric [12,13] or isoenergetic nonequilibrium algorithms. Because the least action principle applies to quantum systems too, there is potential for developing new methods for treating nonequilibrium quantum systems [14]. Our specific isokinetic example illustrates the fundamental limitation of Lagrangian mechanics to equilibrium.

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