

## Nonequilibrium molecular dynamics via Gauss's principle of least constraint

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Gauss's principle of least constraint is used to develop nonequilibrium molecular-dynamics algorithms for systems subject to constraints. The treatment not only includes "nonholonomic" constraints—those involving velocities—but it also provides a basis for simulating nonequilibrium steady states. We describe two applications of this new use of Gauss's principle. The first of these examples, the isothermal molecular dynamics of a three-particle chain, can be treated analytically. The second, the steady-state diffusion of a Lennard-Jones liquid, near its triple point, is studied numerically. The measured diffusion coefficient agrees with independent estimates from equilibrium fluctuation theory and from Hamiltonian external fields.

## I. INTRODUCTION

Many-body systems have been simulated by solving Newton's equations of motion, ever since the development of computers. Early constant-energy Newtonian dynamic studies were concerned with the nature of equilibrium, and the approach to it. But, to drive realistic nonequilibrium systems undergoing shear or compressional flows or heat flows, a new kind of *nonequilibrium* molecular dynamics was needed.

About ten years ago, nonequilibrium molecular-dynamics (NEMD) simulations using heat reservoirs and moving boundaries began to be developed, but on a case-by-case basis, without an underlying basic formalism. Very recently, Hoover and Evans discovered that Karl Friedrich Gauss, in 1829, had enunciated a fundamental dynamical principle (Gauss called it *the* most fundamental principle) which can fruitfully be applied to a wide range of irreversible phenomena and used to generate NEMD algorithms. We describe and illustrate our new treatment of Gauss's principle of least constraint.

In dynamical problems "holonomic" constraints are used to restrict *coordinates* only. Such constraints are used to fix bond lengths or angles at average values, thereby avoiding small-amplitude high-frequency motions. The equations of motion for a system with these geometric constraints were written by Ryckaert, Ciccotti, and Berendsen,<sup>1</sup> using Lagrange multipliers. Their numerical method satisfies the constraint equations continuously. Here we point out that this same technique<sup>1</sup> can be generalized to the *nonholonomic* (*velocity-dependent*) case in which the constraint forces can do work on the system. These constrained equations can be found directly from Gauss's principle of least constraint.<sup>2</sup>

This simple extension of the kinds of constraints considered permits us to describe homogeneous nonequilibrium steady states. In characterizing such a state at least two constraints are used. The first "driving" constraint sets the value of the thermodynamic force or flux and the second "stabilizing" constraint fixes a thermodynamic

variable in order to maintain a steady nonequilibrium state. Typically the driving constraint is a strain rate or heat flux, and the stabilizing constraint corresponds to constant energy or constant temperature.<sup>3-5</sup>

A steady irreversible process produces entropy, through irreversible heating or mixing, and must therefore incorporate a compensating mechanism for extracting heat or separating molecular species. Heat is ordinarily removed, by conduction, at isothermal boundaries. However, by using stabilizing constraints to maintain a steady state we can avoid the need for physical boundaries and substantially reduce the dependence of our results on system size. The techniques described here are remarkably flexible, permitting steady states to be maintained either by thermodynamic forces or by the conjugate thermodynamic fluxes.

Because these constraints are novel, we illustrate them first with a familiar system, simple enough for complete analysis: the three-particle Hooke's-law chain. We then apply the same techniques to a complicated many-body problem, the simulation of steady diffusive flow in a model liquid.

## II. GAUSS'S PRINCIPLE OF LEAST CONSTRAINT (REF. 6)

It is not widely appreciated that just over 150 years ago Gauss formulated a mechanics more general than Newton's. Gauss's formulation applies to systems which are subject to constraints, either holonomic or nonholonomic. Gauss stated that the trajectories actually followed would deviate as little as possible, in a least-squares sense, from the unconstrained Newtonian trajectories.<sup>6</sup>

If the constraints do no work on the system then it is possible to prove that Newton's and Gauss's formulations are equivalent.<sup>2</sup> The equivalence holds also in the nonholonomic case with linear homogeneous work-performing constraints.<sup>7-9</sup> But in the general case the "proofs" of Gauss's principle of least constraint require the addition of postulates or assumptions to Newton's equations of

motion. Here we follow Appell<sup>10</sup> and Ray,<sup>8</sup> simply accepting without proof the validity of Gauss's principle.

To reduce Gauss's principle to a form suitable for numerical work, we first introduce constraints into the equations of motion. It is necessary to treat holonomic constraints  $g(r,t)=0$  and nonholonomic constraints  $g(r,\dot{r},t)=0$  separately. In the holonomic case, two differentiations with respect to time give the relation restricting the acceleration  $\ddot{r}$

$$\ddot{r} \frac{\partial g}{\partial r} + 2\dot{r} \frac{\partial^2 g}{\partial r \partial t} + \dot{r}^2 \frac{\partial^2 g}{\partial r^2} + \frac{\partial^2 g}{\partial t^2} = 0 . \quad (1a)$$

In the nonholonomic case only a single time differentiation is required

$$\ddot{r} \frac{\partial g}{\partial \dot{r}} + \dot{r} \frac{\partial g}{\partial r} + \frac{\partial g}{\partial t} = 0 . \quad (1b)$$

In *either* case the acceleration  $\ddot{r}$  is constrained to lie on the constant- $g$  hypersurface by a restriction of the general form

$$n(r,\dot{r},t) \cdot \ddot{r} + w(r,\dot{r},t) = 0 , \quad (2)$$

where the explicit functional forms of  $n$  and  $w$  can be obtained from the imposed constraint  $g$  according to Eqs. (1) above.

The explicit forms of  $n(r,\dot{r},t)$  and  $w(r,\dot{r},t)$  are not essential in the general treatment outlined in Eqs. (3)–(6) below. At all times the dynamical state of the system  $r,\dot{r}$  is confined to the hypersurface which satisfies Eq. (2). If the constraints (1) were absent, then the unconstrained motion of the system calculated from

$$m\ddot{r}_u = F , \quad (3)$$

could leave the constraint hypersurface. Gauss's formulation prevents such a violation by adding an acceleration normal to the surface

$$\ddot{r}_c = \ddot{r}_u - \lambda [n(r,\dot{r},t)/m] \quad (4)$$

with  $\lambda$  chosen to satisfy the restriction (2), and thereby (1)

$$\lambda = (n \cdot \ddot{r}_u + w) / [n \cdot (n/m)] . \quad (5)$$

This added acceleration can be expressed in terms of a constraint force  $F_c$ :

$$\ddot{r}_c = (F + F_c) / m = F/m - \lambda (n/m) , \quad (6)$$

where the instantaneous value of the Lagrange multiplier  $\lambda$  is chosen to satisfy the constraint (1) according to Eq. (5).

There are *many* different ways to project unconstrained accelerations back onto the constrained hypersurface. Gauss's principle of least constraint states that the actual constrained motion should be obtained by the normal projection technique just described. An alternative description of this simple principle is the statement that the mean-square value of the constraint force divided by the particle mass  $\langle F_c^2 / m \rangle$  should be minimized.

### III. APPLICATION TO AN ISOTHERMAL LINEAR CHAIN (REF. 11)

The harmonic one-dimensional chain is a familiar prototype for ordered crystalline solids. Each particle in such

a chain interacts with its neighbors through a Hooke's-law potential. The equations of motion have the form

$$m\ddot{x}_i = \kappa(x_{i+1} - 2x_i + x_{i-1}) , \quad (7)$$

where  $x_{i+1}$  and  $x_{i-1}$  are the coordinates of the particles adjacent to that at  $x_i$ . Because this problem is linear, the various "normal-mode" solutions can be superposed to match any initial conditions (the set of  $x_i$  and  $\dot{x}_i$ ), and to follow the constant-energy dynamical development of the chain in time.

In *nonequilibrium* problems it is convenient to specify isothermal conditions to extract irreversibly generated heat. For that reason we consider here *isothermal*, as opposed to equilibrium isoenergetic, dynamics for the linear chain. The isothermal restriction complicates the microscopic dynamics by imposing a collective constraint, coupling together the previously independent normal modes. But on the other hand, the macroscopic, thermodynamic behavior of the chain is simplified by preventing temperature fluctuations. Our definition of temperature is based on the ideal-gas thermometer; that is, temperature is proportional to the kinetic energy. Thus the constant-temperature constraint has the form

$$g(r,\dot{r},t) = \sum (m\dot{x}^2/2) - E_{\text{kin}} = 0 . \quad (8)$$

The constraint is *nonholonomic*, because it includes velocities, and is also nonlinear. The functions  $n$  and  $w$  corresponding to the isothermal constraint (8) are, respectively,  $m\dot{x}$  and 0. Gauss's principle leads to the constrained accelerations

$$\begin{aligned} \ddot{x}_c &= F/m - \zeta \dot{x} , \\ \zeta &= \sum (F\dot{x}) / \sum m\dot{x}^2 . \end{aligned} \quad (9)$$

The collective variable  $\zeta$  plays the role of a friction coefficient, but it takes on both positive and negative values as time goes on, as required to keep temperature constant. The set of Eqs. (9) cannot be solved analytically, but numerical solutions show that the system is stable and well behaved and that the time-averaged potential energy approaches the equipartition value as the number of masses in the chain increases.

The two-particle chain is uninteresting, because the fixed-kinetic-energy constraint allows no accelerations—the two particles move to infinity at constant speeds. The constrained three-particle chain with fixed center of mass is the simplest interesting problem, because all velocities change with time and cover a broad range of dynamical states (see Fig. 1). We consider the three-particle problem here in detail. We use displacement coordinates (measured relative to a minimum-energy configuration) and periodic boundaries. We have the restrictions

$$x_1 + x_2 + x_3 = 0 , \quad (10a)$$

$$\dot{x}_1 + \dot{x}_2 + \dot{x}_3 = 0 , \quad (10b)$$

$$\dot{x}_1^2 + \dot{x}_2^2 + \dot{x}_3^2 = 2E_{\text{kin}}/m . \quad (10c)$$

The dynamical state of the three-mass system  $\{x_1, x_2, x_3, \dot{x}_1, \dot{x}_2, \dot{x}_3\}$  can then be described by three independent variables:  $x_1$ ,  $x_2$ , and  $\dot{x}_1$ , for instance. The remaining coordinates and velocities follow from the constants of the motion (10).

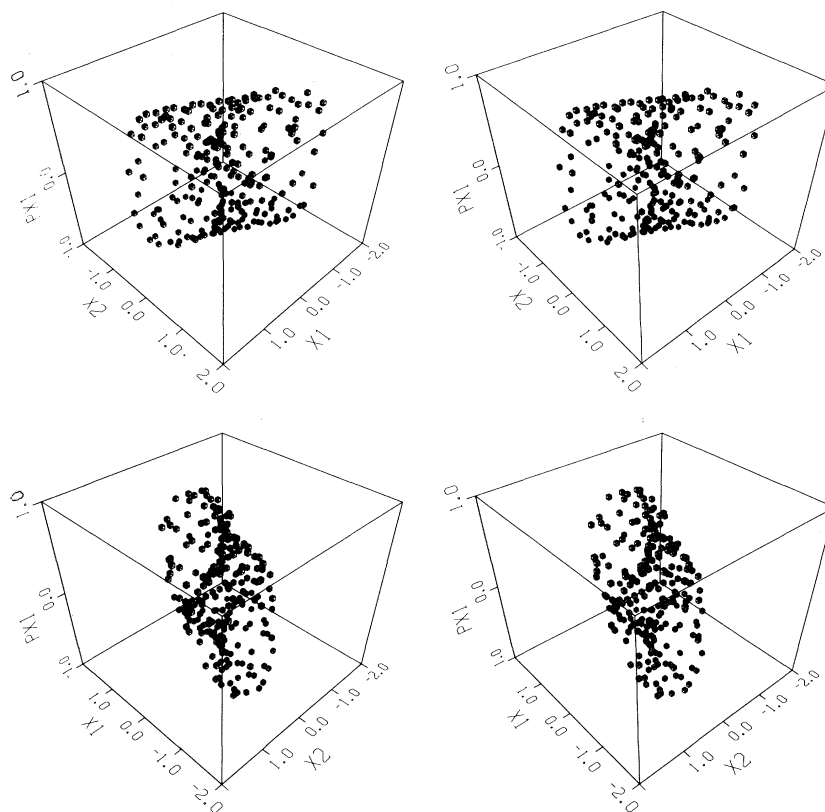


FIG. 1. Two stereo views of the motion of a three-particle isothermal chain. Discrete points  $x_1$ ,  $x_2$ ,  $m\dot{x}_1$  corresponding to a numerical solution of Eqs. (11) of the text are plotted. The corresponding Newtonian chain would describe an ellipse in this space.

The isothermal equations of motion then become

$$\begin{aligned} m\ddot{x}_1 &= -3\kappa x_1 - \zeta m\dot{x}_1, \\ m\ddot{x}_2 &= -3\kappa x_2 - \zeta m\dot{x}_2, \\ \zeta &= -3\kappa[x_1\dot{x}_1 + x_2\dot{x}_2 + (x_1 + x_2)(\dot{x}_1 + \dot{x}_2)]/2E_{\text{kin}}. \end{aligned} \quad (11)$$

The problem can be simplified, analytically, by introducing plane polar coordinates  $r$  and  $\theta$  in place of the particle coordinates  $x_1$  and  $x_2$ :

$$\begin{aligned} r \cos\theta &= \sqrt{3}(x_1 + x_2), \\ r \sin\theta &= x_1 - x_2. \end{aligned} \quad (12)$$

In polar form the problem reduces to one-dimensional (radial) motion in an effective potential which includes the angular momentum. This transformed description of the problem establishes that the isothermal chain dynamics consists of nonlinear oscillations between the two turning points of the effective potential

$$v_{\text{eff}}(r) = A \exp(Br^2)/r^2, \quad (13)$$

where the constants  $A$  and  $B$  depend upon the initial conditions.

A typical series of representative points  $(x_1, x_2, m\dot{x}_1)$ , from a numerical solution of equations (11), is displayed in Fig. 1. The motion is relatively complex, compared to

the Newtonian solution, which is an ellipse in the same space.

Gauss's principle provides a unique solution to the isothermal initial-value problem. As noted above there are *many* other motions which preserve the kinetic energy. For instance, consider the Lagrangian equations of motion involving the nonphysical momentum  $p_x$

$$\begin{aligned} p_x &= m\dot{x}(1 + \lambda), \\ \dot{p}_x &= -3\kappa x. \end{aligned} \quad (14)$$

These equations, with the constraint (10) governing the time development of  $\lambda$ , are identical to the constrained Gaussian set (11) if the Lagrange multiplier vanishes, so that  $p_x$  is equal to  $m\dot{x}$ . Then the Lagrangian and Gaussian values of  $\ddot{x}$  differ. In any other case, Eqs. (14) lead to different values of  $\ddot{x}$  from the same initial conditions. Because  $p_x$  is not a physical momentum the initial conditions  $\{x, \dot{x}\}$  are insufficient to specify a well-posed problem. Once a particular initial choice of  $\lambda$  has been made, the motion can again be studied in polar coordinates, with an effective potential which is the reciprocal of a sixth-order polynomial in  $r$ . The resulting Lagrangian dynamics, Eq. (14), resembles qualitatively the Gaussian dynamics of Fig. 1. The two approaches can be made to coincide by

continuously forcing the Lagrange multiplier in Eq. (14) to vanish.

#### IV. HAMILTONIAN ALGORITHM FOR SELF-DIFFUSION

To complement the periodic and homogeneous treatments of momentum<sup>12</sup> and heat flows<sup>13</sup> we develop here a Hamiltonian method for determining the self-diffusion coefficient  $D$ .  $D$  can alternatively be calculated from the equilibrium Green-Kubo expression

$$D = \int_0^\infty \langle \dot{x}(0)\dot{x}(t) \rangle_{\text{eq}} dt . \quad (15)$$

Many calculations have been based on this method, starting with the hard-sphere calculations of Alder and Wainwright.<sup>14</sup> An alternative approach introduces an external field into the Hamiltonian which couples to a particle property  $q_i$  analogous to electric charge. We call this property "color" rather than "charge" to emphasize that it does not enter into interparticle interactions. The many-body Hamiltonian

$$H_0 = \sum (m\dot{r}^2/2) + \sum \sum \phi \quad (16)$$

has added to it a perturbing external field at time 0

$$H = H_0 - \sum qx E, \quad t > 0 . \quad (17)$$

The external field  $E$  stimulates a current density  $J$

$$J_x = (1/V) \sum qx \dot{x} , \quad (18)$$

analogous to an electric current density. For simplicity we choose  $q_i$  equal to  $-1$  for  $i \leq n/2$  and  $q_i$  equal to  $+1$  for the remaining particles. The linear-response theory<sup>15</sup> establishes that the limiting small-field nonequilibrium current density can be written in terms of an equilibrium color conductivity memory function  $\sigma$ :

$$\langle J(t) \rangle_{\text{ne}} = \int_0^t \sigma(t - \Delta t) E(\Delta t) d\Delta t , \quad (19)$$

$$\sigma(t) = (V/kT) \langle J(0)J(t) \rangle_{\text{eq}} .$$

The current-density autocorrelation function is simply related to the velocity autocorrelation function in Eq. (15). This is because  $\langle x_j \rangle$  is  $-x_1/(N-1)$  for  $j=2,3,\dots,N$ , which can be used to show that the steady color conductivity is proportional to the self-diffusion coefficient  $D$

$$\sigma = \int_0^\infty \sigma(t) dt = N^2 D / [(N-1)VkT] . \quad (20)$$

Thus the self-diffusion coefficient can be determined by carrying out a series of constant-field simulations and extrapolating the resulting conductivities to the zero-field limit. See Fig. 2.

The work done by the external field would normally cause the system to heat up at a rate proportional to  $E^2$  in the small-field limit. This heating can be eliminated by carrying out the calculation at fixed temperature. In the numerical work described in Sec. VI we do this by rescaling the  $y$  and  $z$  components of the velocity distribution to maintain the corresponding second moments at fixed values.<sup>16,17</sup>

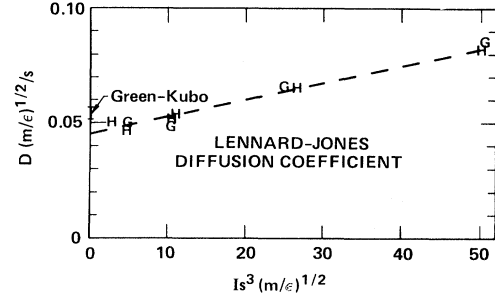


FIG. 2. Self-diffusion coefficient for a Lennard-Jones liquid at a reduced density  $Ns^3/V=0.85$  and reduced temperature  $kT/\epsilon=1.08$ . Calculations according to Gaussian dynamics and using Hamiltonian external fields are indicated by  $G$  and  $H$ , respectively. Green-Kubo calculation, from Ref. 18, is probably an overestimate, as explained in Sec. VI of the text.

#### V. GAUSSIAN ALGORITHM FOR SELF-DIFFUSION

The diffusion problem can be treated directly using Gauss's principle of least constraint. A driving constraint  $g_d$  provides a constant current, and a stabilizing constraint  $g_s$  provides constant  $y$  and  $z$  temperatures

$$\begin{aligned} g_d &= \sum (q\dot{x}) - I = 0 , \\ g_s &= \sum m(\dot{y}^2 + \dot{z}^2)/2 - NkT = 0 . \end{aligned} \quad (21)$$

The equations of motion include contributions from the two Lagrange parameters used to satisfy these constraints

$$\begin{aligned} m\ddot{x} &= F_x - \lambda_d q , \\ m\ddot{y} &= F_y - \lambda_s m\dot{y} , \\ m\ddot{z} &= F_z - \lambda_s m\dot{z} . \end{aligned} \quad (22)$$

The multipliers can be identified explicitly by multiplying the equations of motion (22) by  $(q/m)$ ,  $\dot{y}$ , and  $\dot{z}$ , and summing over all particles

$$\begin{aligned} \sum (q\ddot{x}) &= \frac{dI}{dt} = 0 = \sum (qF_x/m) - (\lambda_d/m) \sum q^2 , \\ \sum (m\dot{y}\ddot{y} + m\dot{z}\ddot{z}) &= 0 = \sum (\dot{y}F_y + \dot{z}F_z) \\ &\quad - \lambda_s \sum m(\dot{y}^2 + \dot{z}^2) . \end{aligned} \quad (23)$$

Thus the Lagrange multipliers are functions of time which depend only upon the particle colors, velocities, and forces

$$\begin{aligned} \lambda_d &= \sum (qF_x) / \sum (q^2) , \\ \lambda_s &= \sum (\dot{y}F_y + \dot{z}F_z) / \sum m(\dot{y}^2 + \dot{z}^2) . \end{aligned} \quad (24)$$

The forces of constraint associated with the current density and the temperature do work on the system at the rates

$$P_d = \sum (qF_x) \sum (q\dot{x}) / \sum (q^2)$$

and

$$P_s = - \sum (\dot{y}F_y + \dot{z}F_z) , \quad (25)$$

respectively.

The color conductivity can be determined either from the driving power  $P_d$  associated with maintaining the current or with the stabilizing power  $P_s$  used to keep the temperature constant:

$$\sigma = I_0^2/V\langle P_d \rangle_{ne} = -I_0^2/V\langle P_s \rangle_{ne} . \quad (26)$$

The angular brackets in Eq. (26) indicate long-time steady-state averages. For short times  $P_d$  tends to exceed  $-P_s$  by the rate at which energy is being stored in the system through its developing nonequilibrium distribution function.

Although this nonequilibrium diffusion problem is a relatively simple one, it is clear that Gauss's principle makes it possible to formulate many problems in a convenient way. The principle is particularly valuable in establishing nonequilibrium steady states suitable for theoretical analysis.

## VI. SIMULATION RESULTS

Levesque and Verlet<sup>18</sup> determined the self-diffusion coefficient for a dense liquid composed of 864 particles interacting with the Lennard-Jones potential

$$\phi = 4\epsilon[(s/r)^{12} - (s/r)^6] . \quad (27)$$

They used the Green-Kubo formula [Eq. (15)] and considered a temperature  $1.08\epsilon/k$  and number density  $(N/V)=0.85/s^3$  close to the liquid triple point. In our 108-particle calculations, at this same thermodynamic-state point, we truncate the potential at  $r=2.5s$ .

Calculations using the Hamiltonian algorithm described in Sec. IV have been carried out by Snook, Evans, and Isbister.<sup>19</sup> For comparison with those results we have solved the Gaussian equations of motion (using a fifth-order predictor-corrector "Gear" integration) with a time step of  $0.002(m/\epsilon)^{1/2}s$ . The constraints maintained constant current and temperature to an accuracy of plus or minus 0.05% in 10000 time steps. Typical run lengths were 15000 steps.

Figure 2 shows the diffusion coefficient [related to the color conductivity by Eq. (20)] as a function of current. It is noteworthy that the two nonequilibrium methods are self-consistent within the statistical uncertainties. The equilibrium Green-Kubo conductivity, which appears to exceed the nonequilibrium conductivities, is probably slightly overestimated. The intermediate-time negative velocity correlation function was truncated in carrying out the Green-Kubo calculation according to Eq. (15).

The Gaussian method is more efficient than the Hamiltonian one because the transition time required to reach steady-state conditions is substantially reduced. In the Hamiltonian simulation approximately 10000 time steps are necessary to attain the steady state from an initial equilibrium state. The accuracy with which the constraints are satisfied, and the balance between the work

done and heat rejected, are convenient checks on the numerical work.

## VII. CONCLUSION

In classical mechanics, constraints are used to simplify the analysis of dynamical systems. These constraints can be removed entirely if a full analysis is made of the interaction of the system and its surroundings. Constraints are used to replace the (possibly very complex) dynamics of the surroundings by their net effect (through the forces of constraint) on the system of interest. Gauss's principle of least constraint provides us with a systematic means for correctly formulating the equations of motion in such constrained systems.

Gauss's principle is ideal for developing nonequilibrium computer simulations. It allows us to project out of the motion the degrees of freedom corresponding to external reservoirs, replacing these thermodynamic baths by forces of constraint. We believe that the fundamental properties of nonequilibrium steady states can best be determined in this way.

There are several indications that Gauss's principle, as an extension of Newtonian mechanics, is consistent with statistical mechanics and kinetic theory. First, the isothermal dynamics is consistent with the Gibbs canonical ensemble.<sup>3</sup> A set of systems initially distributed canonically in the phase space remains distributed canonically, despite the changes in the energies of the systems making up the ensemble. Second, the isothermal dynamics, applied to a low-density shear-flow problem, predicts exactly the same shear and normal stresses as those derived from the Burnett-level solution of the Boltzmann equation.<sup>20</sup> Finally, equilibrium configurational properties, calculated using the isothermal equations of motion, can be shown to agree with the same properties calculated using the canonical ensemble of Gibbs.<sup>5</sup>

Here we have stressed the application of Gaussian dynamics to nonequilibrium steady states. It is evident that similar calculations can be applied to nonsteady problems and to systems in other ensembles, such as constant pressure.<sup>21</sup>

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