

## Constant-pressure equations of motion

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Some of the differences among several alternative formulations of constant-pressure molecular dynamics are described. The formulations all agree in the large-system limit, but differ for small systems.

Several times during the past year I have been asked to explain the difference between the Nosé-Andersen<sup>1-4</sup> "isobaric-isothermal" equations of motion (in which pressure and kinetic energy fluctuate) and the closely related equations I described in my later work on the Nosé oscillator.<sup>5</sup> This Brief Report answers that question.

In both cases the motivating idea was the same—to use equations of motion which can generate the phase-space density typical of the Gibbsian isobaric-isothermal partition function. Such a goal is different from that pursued, at about the same time, by Evans and Morriss<sup>6</sup> and Abraham,<sup>7</sup> who independently developed a third set of equations which instead make the instantaneous pressure  $P$  a constant of the motion:

$$\dot{P}=0, \quad PV \equiv \left[ \sum (p^2/m) + \sum \sum (r \cdot F) \right] / D. \quad (1)$$

In Eq. (1) the pressure  $P$  is held constant by calculating an instantaneous infinite-frequency bulk modulus and adjusting the volume  $V$  to satisfy the condition  $\dot{P}=0$ . In Eq. (1) the  $N$ -particle volume, usually periodic, is  $D$  dimensional. The first sum runs over all  $N$  particles, each of mass  $m$ . The double sum includes each pair of particles once. The nearest-image convention is used in calculating the scalar dot product of the pair's separation  $r$  and the force  $F$ .

In Gibbsian statistical mechanics the usual "isobaric" ensembles allow the instantaneous pressure  $P$  defined by (1) to fluctuate around a specified mean value  $P_0$ . The probability density in the isobaric-isothermal  $N-P_0-T$  ensemble is proportional to the exponential of a reduced instantaneous enthalpy,  $(E+P_0V)/k_B T$ , where  $k_B$  is Boltzmann's constant and  $T$  is a specified temperature, around which the instantaneous temperature  $\sum (p^2/mNDk_B)$  fluctuates. The volume  $V$  and the kinetic energy  $K$  both vary with time, as do also the coordinates  $q$  and momenta  $p$  appearing in the internal energy  $E(q,p)$ .

In carrying out any isobaric-ensemble simulation it is convenient to use  $D$ -dimensional vector coordinates  $x$ , the components of which range from 0 to 1 in each of the  $D$  space directions. These coordinates are independent of the volume  $V$ , which changes as a function of time. In Refs. 1-5 volume is used as an independent variable; strain, proportional to the logarithm of the volume, could equally well have been used. Likewise, to describe the

change of the volume with time, either  $\dot{V}$  or the strain rate  $\dot{\epsilon} = \dot{V}/V$  can be used. Andersen and Nosé chose  $\dot{V}$ . I chose  $\dot{\epsilon}$ . Any of the combinations  $V-\dot{V}$ ,  $V-\dot{\epsilon}$ ,  $\epsilon-\dot{\epsilon}$ , and  $\epsilon-\dot{V}$  is satisfactory but each of the four sets of variables leads naturally to a unique set of motion equations. Of course it is true that any of the four resulting sets of motion equations could be expressed in terms of any of the four sets of variables. Thus the chosen independent variables influence, but do not determine uniquely, the equations of motion.

One satisfactory complete set of variables for isobaric-isothermal simulations is  $x-p-\zeta-V-\dot{\epsilon}$ . Nosé discovered that by using a new friction coefficient variable  $\zeta$  the isobaric-isothermal ensemble could be generated with molecular dynamics. In Nosé's formulation the momenta change not only through their adiabatic coupling to the strain rate but also through their coupling to a heat bath described by  $\zeta$  and a parameter  $Q$  with units of action times time. I showed<sup>5</sup> that a corresponding isobaric-isothermal phase-space density  $f(x,p,\zeta,V,\dot{\epsilon})$  is proportional to

$$V^{N-1} \exp\{[-\Phi - K - P_0 V - (Q\zeta^2/2)]/k_B T - D(\dot{\epsilon}\tau)^2/2\}.$$

I pointed out in Ref. 5 that the equations of motion

$$\begin{aligned} \dot{x} &= p/mV^{1/D}, \\ \dot{p} &= F - (\zeta + \dot{\epsilon})p, \\ \dot{\zeta} &= 2(K - K_0)/Q, \\ \dot{V} &= DV\dot{\epsilon}, \end{aligned} \quad (2)$$

when supplemented by an evolution equation for the strain rate  $\dot{\epsilon}$

$$\dot{\epsilon} = (P - P_0)V/kT\tau^2, \quad (3)$$

satisfy Liouville's probability-conservation equation:

$$\begin{aligned} 0 &= \partial f / \partial t \\ &+ f(\partial \dot{x} / \partial x + \partial \dot{p} / \partial p + \partial \dot{\zeta} / \partial \zeta + \partial \dot{V} / \partial V + \partial \dot{\epsilon} / \partial \epsilon) \\ &+ \dot{x} \partial f / \partial x + \dot{p} \partial f / \partial p + \dot{\zeta} \partial f / \partial \zeta + \dot{V} \partial f / \partial V + \dot{\epsilon} \partial f / \partial \epsilon. \end{aligned} \quad (4)$$

On the other hand, the original Andersen-Nosé equations of motion use  $\dot{V}$  rather than  $\dot{\epsilon}$  as an independent variable. The equation of motion for  $\dot{V}$  is

$$\ddot{V} = (P - P_0) / M. \quad (5)$$

In Eq. (5)  $M$  is a parameter with units mass  $\times$  (length) $^{2-2D}$ . This equation also leads to a probability density satisfying an analog of the Liouville equation (4). But the extended phase-space density is slightly different. For the Andersen-Nosé equations the equilibrium phase-space density  $f(x, p, \zeta, V, \dot{V})$  turns out to be proportional to

$$V^N \exp[(-\Phi - K - P_0 V) / k_B T] \\ \times \exp[-(Q\zeta^2 + MD\dot{V}^2) / 2k_B T].$$

It is clear that after integrating over the strain rate  $\dot{V}$  the two probability densities differ by one power of the volume  $V$ , but otherwise give exactly the same phase space density in the variables,  $x - p - \zeta - V$ . Both Eqs. (3) and (5), as well as the alternatives using the pairs  $\epsilon - \dot{V}$

and  $\epsilon - \dot{\epsilon}$ , are equally valid representations of the isobaric-isothermal ensemble. It is possible that one of these five formulations might be "best" for systems with only a few degrees of freedom, but the differences between the formulations are relatively small, of order  $(1/N)$ . If, as is usual in molecular dynamics simulations, the center of mass is kept fixed, then the number of independent  $x-p$  pairs is reduced by 1 and the  $N$  in both probability densities is reduced to  $N - 1$ .

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<sup>3</sup>S. Nosé, *Mol. Phys.* **52**, 255 (1984).

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<sup>6</sup>D. J. Evans and G. P. Morriss, *Chem. Phys.* **77**, 63 (1983).

<sup>7</sup>F. F. Abraham, *J. Vac. Sci. Technol. B* **2**, 534 (1984).