

## Isothermal molecular-dynamics ensembles

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S. Nosé [Mol. Phys. **52**, 255 (1984); J. Chem. Phys. **81**, 511 (1984)] has developed a form of molecular dynamics that generates the canonical ensemble. Since molecular-dynamics calculations are carried out at constant total linear momentum, we investigate the necessary modifications in Nosé's theory when the constraint of constant total linear momentum is imposed. We show that Nosé's theory can be modified so that it generates phase-space trajectories corresponding to a constant-momentum canonical ensemble with zero total momentum. We also present an exact treatment of the statistical mechanics of this constant-momentum canonical ensemble, including expressions relating averages to thermodynamic variables and formulas involving thermodynamic response functions which are often used in molecular-dynamics calculations.

### I. INTRODUCTION

In molecular-dynamics simulations one numerically solves the classical equations of motion for the trajectories of a system of  $N$  particles interacting through a potential  $U$ , occupying a volume  $V$ , and having an energy  $E$ . If the system is in equilibrium, then these trajectories generate a microcanonical or  $EVN$  ensemble. It is well known that in molecular-dynamics calculations, the total linear momentum  $\mathbf{M}$  of the system is a constant of the motion; the trajectories actually generate an  $EVNM$  ensemble. The fact that molecular dynamics generates an ensemble which is a special case of a microcanonical ensemble with constant total momentum was pointed out in an early paper by Lebowitz, Percus, and Verlet<sup>1</sup> and has been stressed by Wood,<sup>2</sup> who refers to ensembles for which the total linear momentum is constant as molecular-dynamics ensembles.

Recently, we<sup>3</sup> have presented a detailed treatment of the statistical mechanics of the  $EVNM$  ensemble including the exact derivation of various formulas involving thermodynamic response functions. Also presented was a numerical comparison of the results obtained using these exact formulas with the results obtained using fluctuation formulas usually employed in molecular-dynamics calculations. The numerical comparison was carried out using a pseudopotential model for sodium. For the system investigated, 432 sodium atoms interacting through a pseudopotential, the results obtained using different formulas were the same within the accuracy of the calculation.

Nosé<sup>4,5</sup> has developed a technique for carrying out molecular-dynamics calculations such that the trajectories generate an isothermal or canonical ensemble. The most detailed check that Nosé's theory generates a canonical ensemble is probably the fluctuation formula calculation of elastic constants by Ray and co-workers<sup>6,7</sup> using Nosé's theory, and a comparison of the results obtained with accurate Monte Carlo calculations of these same quantities; the Monte Carlo configurations generate the canonical or  $TVN$  ensemble, where  $T$  is the temperature of the reservoir. In this elastic-constant calculation,

the same results were obtained using the Monte Carlo method and Nosé's form of molecular dynamics, within the accuracy of the calculations. These calculations were carried out using a nearest-neighbor Lennard-Jones model system for which accurate Monte Carlo results were available for comparison.

In the literature, Nosé's theory has been associated with the  $TVN$  or canonical ensemble.<sup>4-7</sup> However, since the total linear momentum is a constant of the motion in molecular-dynamics calculations, the trajectories of this theory must generate a  $TVNM$  canonical ensemble. We shall show, later in this paper, that with minor but necessary modifications in the Nosé Hamiltonian, the trajectories of this theory do in fact generate a  $TVNM$  ensemble if the linear momentum is chosen to be zero. Since molecular-dynamics calculations are normally carried out with zero total momentum, the fact that the total momentum must be zero in Nosé's theory, for it to correspond to an equilibrium ensemble, is not a practical limitation.

In Sec. II of this paper we present the theory of the  $TVNM$  ensemble, while in Sec. III we shall show the modifications that are necessary in Nosé's theory to make it consistent with the  $TVNM$  ensemble. In Sec. IV we present a discussion of other constant-momentum isothermal ensembles that are generated in molecular dynamics; these include isothermal-isobaric and isothermal-isotension ensembles. Finally, in Sec. V we present our conclusions.

### II. $TVNM$ ENSEMBLE

We consider a system described by the Hamiltonian  $\mathcal{H}(x,p)$ . The  $TVN$  canonical-ensemble probability density has the form

$$W_c(x,p) = Ce^{-\mathcal{H}/k_B T}, \quad (2.1)$$

where  $C$  is a normalization constant, and  $T$  is the reservoir temperature. If the total linear momentum of the system is constant, then we are dealing with the  $TVNM$  or canonical molecular-dynamics ensemble which has the

probability density modified to the form

$$W_c(x,p) = C e^{-\mathcal{H}/k_B T} \delta \left[ \mathbf{M} - \sum_a \mathbf{p}_a \right], \quad (2.2)$$

that is, only linear momenta that satisfy the conservation law are allowed. The *TVNM* probability density given in Eq. (2.2) may be derived by the usual procedure of partitioning an isolated system, described by the microcanonical *EVNM* ensemble, into two parts 1+2 and allowing the exchange of energy across the partition dividing the two parts. In the limit, as one of the parts becomes much larger than the other, the larger part becomes a thermal reservoir for the smaller, which has the probability density given in Eq. (2.2). Another way to arrive at Eq. (2.2) is to carry out a Laplace transform on the probability density  $W_m$  of the microcanonical *EVNM* ensemble. The latter has the form

$$W_m(x,p) = C \delta(E - \mathcal{H}) \delta \left[ \mathbf{M} - \sum_a \mathbf{p}_a \right]. \quad (2.3)$$

Multiplying Eq. (2.3) by  $e^{-E/k_B T}$  and integrating over the energy, we again obtain Eq. (2.2).

The average value  $\langle A \rangle$  of any dynamical variable  $A(x,p)$  in the *TVNM* ensemble has the form

$$\langle A \rangle = \frac{\int A e^{-\mathcal{H}/k_B T} \delta \left[ \mathbf{M} - \sum_a \mathbf{p}_a \right] d^{3N}x d^{3N}p}{\int e^{-\mathcal{H}/k_B T} \delta \left[ \mathbf{M} - \sum_a \mathbf{p}_a \right] d^{3N}x d^{3N}p}. \quad (2.4)$$

For example, for the kinetic energy  $K = \sum_a \mathbf{p}_a^2 / 2m$ , we obtain, using Eq. (2.4),

$$\langle K \rangle = \frac{M^2}{2Nm} + \frac{3}{2}(N-1)k_B T, \quad (2.5)$$

where we have used the Fourier transform of the  $\delta$  function in order to carry out the momentum integrals in Eq. (2.4). If the total momentum of the system is chosen to be zero ( $\mathbf{M}=0$ ), then  $\langle K \rangle$  is the average internal kinetic energy of the system  $\langle K \rangle |_{\mathbf{M}=0}$ ,

$$\langle K \rangle |_{\mathbf{M}=0} = \frac{3}{2}(N-1)k_B T. \quad (2.6)$$

From Eq. (2.5) or (2.6), we see that one effect of the constant-linear-momentum constraint, as compared to the *TVN* result, is the reduction of the number of degrees of freedom by 3 in the average internal kinetic energy, that is,  $N \rightarrow N-1$ . Equation (2.6) implies that results obtained in the *TVNM* ensemble are not necessarily the same as results obtained in the *TVN* ensemble; however, for large numbers of particles, there will not be significant numerical differences between the values obtained in these two ensembles. The correspondence between the *TVNM*- and *TVN*-ensemble results closely parallels the correspondence found between the *EVNM* and *EVN* ensembles in Ref. 3; Eqs. (2.5) and (2.6) have the same form in the *EVNM* ensemble. We note, however, that the proof of these correspondences is considerably different.

The canonical partition function  $Z(T, V, N, \mathbf{M})$  has the form

$$Z(T, V, N, \mathbf{M}) = \int e^{-\mathcal{H}/k_B T} \delta \left[ \mathbf{M} - \sum_a \mathbf{p}_a \right] d^{3N}x d^{3N}p / C_N, \quad (2.7)$$

where  $C_N$  is a constant. The momentum integrals in Eq. (2.7) may be carried out, and one finds a reduced form of the partition function

$$Z(T, V, N, \mathbf{M}) = e^{-M^2/(2Nm k_B T)} (2\pi m k_B T)^{3(N-1)/2} \times \int e^{-U/k_B T} d^{3N}x / (N^{3/2} C_N). \quad (2.8)$$

Note that even in the limit when  $\mathbf{M}=0$  this partition function differs from the usual canonical ensemble or *TVN* partition function which has the form

$$Z(T, V, N) = (2\pi m k_B T)^{3N/2} \int e^{-U/k_B T} d^{3N}x / C'_N, \quad (2.9)$$

where  $C'_N$  is a constant. It is clear from Eq. (2.8) that any dynamical variable which depends only upon the configuration-space coordinates  $x$  will have the same average in the *TVN* and *TVNM* ensembles; for example, the average potential energy will be the same in both ensembles.

A further connection to thermodynamics is made through the relationship of  $Z$  to the Helmholtz free energy  $F(T, V, N, \mathbf{M})$

$$F = -k_B T \ln Z. \quad (2.10)$$

The expression for the pressure may be obtained by differentiation of  $F$  with respect to  $V$ ;  $P = -(\partial F / \partial V)_T$ , which yields

$$P = \frac{N k_B T}{V} - \left\langle \frac{\partial U}{\partial V} \right\rangle. \quad (2.11)$$

This is the same expression for the pressure as that obtained in the *EVNM* ensemble<sup>3</sup> and in the *TVN* ensemble. It is interesting to note that the pressure cannot be calculated as  $-\langle \partial \mathcal{H} / \partial V \rangle$ , since this is inconsistent with the result one obtains using the thermodynamic relation  $P = -(\partial F / \partial V)_T$ ; the reason for this is the linear-momentum constraint.

Various fluctuation formulas that are characteristic of the *TVNM* ensemble may be derived by differentiation of the partition function or differentiation of selected average values. Differentiation of the average values of the Hamiltonian  $\langle \mathcal{H} \rangle$  yields the well-known formula for the isometric heat capacity  $C_V$ ,

$$\frac{C_V}{k_B} = \frac{1}{(k_B T)^2} (\langle \mathcal{H}^2 \rangle - \langle \mathcal{H} \rangle^2) = \delta(\mathcal{H}^2) / (k_B T)^2. \quad (2.12)$$

If we perform the momentum integrals in Eq. (2.12), then  $C_V$  can be expressed in terms of potential-energy fluctuations

$$\frac{C_V}{k_B} = \frac{3}{2}(N-1) + \delta(U^2) / (k_B T)^2. \quad (2.13)$$

If  $N - 1$  is replaced by  $N$  in Eq. (2.13), then we obtain the  $TVN$  fluctuation formula for the isometric heat capacity. The fluctuation formula for the temperature coefficient of pressure,  $\gamma = (\partial P / \partial T)_V$ , in the  $TVNM$  ensemble takes the form

$$\gamma = \frac{Nk_B}{V} - \delta \left[ U \frac{\partial U}{\partial V} \right] / k_B T^2, \quad (2.14)$$

which is the same result as in the  $TVN$  ensemble. As a final example, we state the fluctuation formula for the isothermal bulk modulus

$$B_T = \frac{Nk_B T}{V} + V \left\langle \frac{\partial^2 U}{\partial V^2} \right\rangle - V \delta \left[ \frac{\partial U}{\partial V} \right]^2 / k_B T, \quad (2.15)$$

which is again the same as the result in the  $TVN$  ensemble.

As mentioned in the Introduction, the importance of the  $TVNM$ -ensemble results presented in this section is the connection with Nosé's isothermal form of molecular dynamics. We shall discuss this connection in detail in Sec. III.

### III. NOSÉ'S ISOTHERMAL MOLECULAR DYNAMICS

Nosé's molecular dynamics is defined by the Hamiltonian<sup>4,5</sup>

$$\mathcal{H}_1 = \sum_a \frac{\pi_a^2}{2mf^2} + U + \frac{P_f^2}{2\mathcal{M}} + (3N + 1)k_B T \ln(f), \quad (3.1)$$

where  $f$  is a mass scaling variable,  $P_f$  is the Nosé momentum conjugate to  $f$ ,  $\pi_a$  is the momentum conjugate to the particle position  $x_a$ ,  $T$  is the preassigned temperature of the reservoir, and  $\mathcal{M}$  is a mass introduced in order to have a dynamical equation for  $f$ . The  $\ln(f)$  term in Eq. (3.1) is the potential energy for the Nosé's variable  $f$ . The motivation for Nosé's Hamiltonian is discussed in Refs. 4 and 5 and will not be repeated. The

conjugate variables for the Nosé Hamiltonian are  $(x, \pi)$  and  $(f, P_f)$ . The equations of motion which follow from Eq. (3.1) have the form

$$mf^2 \ddot{x}_a = - \frac{\partial U}{\partial x_a} - 2mf \dot{f} \dot{x}_a, \quad (3.2a)$$

$$\mathcal{M} \ddot{f} = 2K/f - (3N + 1)k_B T/f. \quad (3.2b)$$

The Hamiltonian, Eq. (3.1), is invariant under translations in time and in space. These invariances of  $\mathcal{H}_1$  lead to conservation of energy  $\mathcal{H}_1 = \text{const}$  and to conservation of linear momentum  $\sum_a \pi_a = \mathbf{M}_n = \text{const}$ , where  $\mathbf{M}_n$  stands for the constant canonical momentum. Therefore, the Hamiltonian, Eq. (3.1), generates an  $EVNM_n$  ensemble with probability density given by [see Eq. (2.3) and Ref. 3]

$$W(x, \pi, f, P_f) = \delta(E_1 - \mathcal{H}_1) \delta \left[ \mathbf{M}_n - \sum \pi_a \right]. \quad (3.3)$$

In the Nosé approach, the microcanonical-ensemble average of a function of position  $x_a$  and the physical momentum,  $\mathbf{p}_a = \pi_a/f$ , using Eq. (3.3), is related to the canonical-ensemble average of this same function. The physical momentum of the particle is defined such that the kinetic energy of the particle, the first term in the Hamiltonian, Eq. (3.1), is given by the conventional expression  $K = \sum_a p_a^2 / (2m)$ . In order for the Nosé Hamiltonian to generate an ensemble with constant physical momentum, we must have  $\sum_a \mathbf{p}_a = \mathbf{M}_n/f = \mathbf{M} = \text{const}$ ; the only way for this latter condition to hold is for the total momentum to be zero, since  $\mathbf{M}_n$  is constant and  $f$  varies with time. Thus, in order for Nosé's theory to generate a canonical molecular-dynamics ensemble, the total momentum must be zero. This means that the probability density in Eq. (3.3) takes the form

$$W(x, \pi, f, P_f) = \delta(E_1 - \mathcal{H}_1) \delta \left[ \sum_a \pi_a \right]. \quad (3.4)$$

Using this probability density, the average value of any function of the position and the physical momentum  $A(x, \pi/f)$  can be written as a microcanonical average via

$$\langle A \rangle = \frac{\int A(x, \pi/f) \delta(E_1 - \mathcal{H}_1) \delta \left[ \sum_a \pi_a \right] d^{3N}x d^{3N}\pi df dP_f}{\int \delta(E_1 - \mathcal{H}_1) \delta \left[ \sum_a \pi_a \right] d^{3N}x d^{3N}\pi df dP_f}. \quad (3.5)$$

If we now replace the Nosé potential-energy term  $(3N + 1)k_B T \ln(f)$  in Eq. (3.1) by

$$[3(N - 1) + 1]k_B T \ln(f),$$

then the average value in Eq. (3.5) can be reduced, by using the change of variables  $\mathbf{p}_a = \pi_a/f$  and carrying out the same steps as in Nosé,<sup>4,5</sup> to the form

$$\langle A \rangle = \frac{\int A(x, p) e^{-\mathcal{H}/k_B T} \delta \left[ \sum_a \mathbf{p}_a \right] d^{3N}x d^{3N}p}{\int e^{-\mathcal{H}/k_B T} \delta \left[ \sum_a \mathbf{p}_a \right] d^{3N}x d^{3N}p}, \quad (3.6)$$

where  $\mathcal{H} = \sum_a p_a^2 / (2m_a) + U$  is the particle Hamiltonian.

The right-hand side of Eq. (3.5) is just the  $TVNM$ -ensemble average of the dynamical variable  $A(x, p)$ , with the total momentum  $\mathbf{M} = 0$ . Therefore, averages calculated using the trajectories given by solving the equations of motion, Eqs. (3.2), [with  $N$  replaced by  $N - 1$  in Eq. (3.2b) and  $\sum_a \pi_a = 0$ ], are equal to  $TVNM$  canonical-ensemble averages with  $\mathbf{M} = 0$ .

It is important to note that since the Nosé Hamiltonian conserves the total linear momentum, it must generate an ensemble with the total momentum constant and, in fact, the constant must have the value zero in order to derive

Eq. (3.6) from Eq. (3.5). The fact that the momentum must be zero is not a practical limitation, since molecular-dynamics calculations are usually carried out with the total momentum being zero.

#### IV. OTHER ISOTHERMAL ENSEMBLES

In the  $TVNM$  ensemble, not only the volume but also the shape and size of the system are held rigid. If the system is in the shape of a parallelepiped spanned by the vectors  $\mathbf{a}$ ,  $\mathbf{b}$ , and  $\mathbf{c}$ , then we may define a matrix by  $h = (\mathbf{a}, \mathbf{b}, \mathbf{c})$ . The isothermal ensemble describing a system with this more general shape is the  $ThNM$  ensemble. The previous discussion relating to the  $TVNM$  ensemble is also valid for the  $ThNM$  ensemble. The  $ThN$  ensemble has been discussed in detail in Ref. 6 and 7. The introduction of  $h$  into the theory in place of  $V$  is significant, since it allows one to discuss the statistical mechanics of anisotropic solids including a detailed treatment of the elastic properties of the material.<sup>7</sup>

Also, one has available  $TPNM$  and  $TtNM$  forms of molecular dynamics where  $P$  is the constant external pressure applied to the system and  $t$  is the constant external thermodynamic tension applied to the system.<sup>6,7</sup> We shall not present the details of these ensembles.

#### V. CONCLUSIONS

In molecular-dynamics calculations, both the total energy and total linear momentum are constants of the motion. Thus, the statistical ensembles generated by different forms of molecular dynamics must be constant-momentum ensembles. For the microcanonical ensemble, this was recognized by Lebowitz, Percus, and Verlet<sup>1</sup> and pointed out by Wood;<sup>2</sup> however, the exact statistical mechanics of this  $EVNM$  ensemble has only recently been presented.<sup>3</sup>

In a like manner, the newer forms of molecular dynamics, isothermal, isobaric, isotension, etc., must generate constant-momentum ensembles. We have shown that with minor modifications, Nosé's isothermal or canonical-ensemble molecular dynamics can be made consistent with the  $TVNM$  ensemble with  $\mathbf{M}=0$ . The modification is that the coefficient of the Nosé potential is changed from  $3N + 1$  to  $3(N - 1) + 1$ , and the momentum must be chosen to be zero.

We have also presented the basic statistical mechanics of the  $TVNM$  ensemble. In the limit of large particle numbers, the numerical differences between the  $TVN$  and  $TVNM$  ensembles will be small; however, the exact theory should be recognized, and the results for small clusters could be of importance.<sup>8</sup> As a final point, we have also indicated how other forms of isothermal molecular dynamics are associated with constant-momentum statistical ensembles.

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