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# Ensemble corrections for the molecular-dynamics ensemble

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Expressions are derived which relate the averages of a dynamical variable in the molecular-dynamics ensemble and in the generalized canonical ensemble. Fluctuations in the two ensembles are also related. These results make the full equilibrium theory of classical statistical mechanics accessible to evaluation by molecular-dynamics computations.

## I. INTRODUCTION

For ensembles composed of finite systems, the same dynamical variable has different averages in different ensembles. Specifically, for systems containing $N$ particles the average of a given intensive variable is of order 1 in all ensembles, and differences among the various ensemble averages are of order $N^{-1}$. On the other hand, an ensemble average of the fluctuation squared of an intensive variable is of order $N^{-1}$ (unless it vanishes identically), and differences among various ensemble averages are of the same order, namely, $N^{-1}$. These differences are called "ensemble differences," or "ensemble corrections." The general theory for ensemble corrections was discussed by Lebowitz, Percus, and Verlet.[1] However, in applying the theory to the relation between molecular-dynamics and canonical ensembles an error was made.[1] In the present paper, expressions are derived for the relation between averages in the molecular-dynamics ensemble and averages in the generalized canonical ensemble. This result should enhance the usefulness of molecular dynamics in equilibrium studies because it makes the full classical statistical mechanical theory, including fluctuations, accessible to evaluation by molecular-dynamics computations.

In order to accomplish our objective a precise specification of several ensembles is required. The molecular-dynamics ensemble, and its difference from the microcanonical ensemble, was described by Wood.[2] A helpful discussion of the generalized canonical ensemble, a canonical ensemble with nonzero average momentum, was given by Lado.[3] It is necessary to use the generalized canonical ensemble in the present theory because it is the ensemble conjugate to the molecular-dynamics ensemble.

It should be noted that there are other finite-size effects which are not considered in the present paper. In a cluster expansion of the thermodynamic functions, errors of relative order $N^{-1}$ appear for sufficiently large clusters.[4,5] Errors related to the boundary conditions are presumably also present in equilibrium molecular-dynamics evaluations.

## II. ORDINARY CANONICAL ENSEMBLE

A system is a collection of $N$ atoms (or ions) in a volume $V$, and for simplicity, we take the atoms to be alike, with mass $m$. The time-dependent position and momentum of atom $L$ are $\vec{x}_L$ and $\vec{p}_L$, respectively, where $L=1,2,\ldots,N$. The total energy of the system is

$$\mathscr{H}=E_{\text{kin}}+\Phi=\sum_L \vec{p}_L^{\,2}/2m+\Phi\ , \tag{1}$$

where $E_{\text{kin}}$ is the kinetic energy and $\Phi$ is the potential, and the total linear momentum is

$$\vec{\mathscr{M}}=\sum_L \vec{p}_L\ . \tag{2}$$

We assume $\Phi$ depends only on the relative atomic positions and the volume, and that $\mathscr{H}$ is bounded below. The phase of a single system at any time is the set $\{\vec{x}_L,\vec{p}_L\}$, and a dynamical variable is represented by $A=A(\{\vec{x}_L,\vec{p}_L\})$. The ensemble is a collection of systems with a prescribed statistical weight function $W(\{\vec{x}_L,\vec{p}_L\})$; the corresponding partition function is $Z=\text{Tr}W$, and the ensemble average is $\langle A\rangle=Z^{-1}\text{Tr}AW$. The dynamical variable representing a fluctuation is $\delta A=A-\langle A\rangle$. In the present paper we consider only classical statistics, so that noncommutation of operators is of no concern and we consider only ensembles with constant $N$ and $V$, therefore, the notation of constant $N$ and $V$ may be suppressed.

The canonical weight function is proportional to $e^{-\beta\mathscr{H}}$, defined through the parameter $\beta=(kT)^{-1}$, where $k$ is Boltzmann's constant and $T$ is temperature. The partition function is

$$Z(\beta)=a_N\int\cdots\int e^{-\beta\mathscr{H}}\prod_L d\vec{x}_L\,d\vec{p}_L\ , \tag{3}$$

where $a_N$ is a normalization constant related to the range of integration of the position variables. For the example of a fluid or gas $a_N^{-1}=N!h^{3N}$, and the $d\vec{x}_L$ are integrated over the entire volume $V$. The canonical-ensemble average of $A$ is

$$\langle A\,|\,\beta\rangle = Z(\beta)^{-1}a_N \int \cdots \int A e^{-\beta\mathcal{H}} \prod_L d\vec{x}_L d\vec{p}_L \ , \tag{4}$$

and its derivative with respect to $\beta$ satisfies the relation

$$\frac{\partial\langle A\,|\,\beta\rangle}{\partial\beta} = -\langle \delta A\,\delta\mathcal{H}\,|\,\beta\rangle \ . \tag{5}$$

Averaging functions of the atomic momenta gives the results

$$\langle \mathcal{M}_i\,|\,\beta\rangle = 0 \ , \tag{6a}$$

$$\langle \mathcal{M}_i\mathcal{M}_j\,|\,\beta\rangle = NmkT\delta_{ij} \ , \tag{6b}$$

$$\langle E_{\text{kin}}\,|\,\beta\rangle = \tfrac{3}{2}NkT \ , \tag{6c}$$

where subscripts $i$ and $j$ indicate Cartesian components.

It is useful to make a unique connection between thermodynamics and statistical mechanics by defining a single thermodynamic state function in a specific ensemble. For this we take the Helmholtz function $F$ in the canonical ensemble:

$$F = -kT\ln Z(\beta) \ . \tag{7}$$

Thermodynamic functions are then obtained in the usual way from $F$, so that they are uniquely defined and ensemble independent. The entropy is $S=-(\partial F/\partial T)_V$, the internal energy is $U=F+TS$, and for the canonical ensemble we have

$$\langle \mathcal{H}\,|\,\beta\rangle = -\frac{\partial \ln Z(\beta)}{\partial\beta} = U \ . \tag{8}$$

The pressure is defined by $P=-(\partial F/\partial V)_T$, and for the canonical ensemble this becomes

$$P = kT\partial\ln Z(\beta)/\partial V.$$

To express $P$ as an ensemble average we take a specific form of $\Phi$, namely, the general form representing a pseudopotential metal,[6,7]

$$\Phi = \Omega(V) + \sum \phi(r;V) \ , \tag{9}$$

where $\Omega(V)$ is a volume-dependent term (here including the ionization energy), $\phi(r;V)$ is a central potential between two ions separated by a distance $r$, and the sum is over all distinct pairs of ions. Evaluation of $P$ in the canonical ensemble then gives

$$PV = -\frac{d\Omega}{d\ln V} + NkT - \langle \mathcal{W}\,|\,\beta\rangle \ , \tag{10}$$

where $\mathcal{W}$ is the generalized virial function

$$\mathcal{W} = \sum \left[ \frac{\partial\phi}{\partial\ln V} + \frac{1}{3}\frac{\partial\phi}{\partial\ln r} \right] . \tag{11}$$

## III. GENERALIZED CANONICAL ENSEMBLE

To construct a canonical ensemble whose average value of the total momentum $\vec{\mathcal{M}}$ is nonzero, we introduce the additional ensemble parameter $\vec{b}$ and set the weight function proportional to $\exp(-\beta H - \vec{b}\cdot\vec{\mathcal{M}})$. The partition function is then

$$Z(\beta,\vec{b}) = a_N \int \cdots \int \exp(-\beta\mathcal{H} - \vec{b}\cdot\vec{\mathcal{M}}) \prod_L d\vec{x}_L d\vec{p}_L , \tag{12}$$

which can be transformed to

$$Z(\beta,\vec{b}) = \exp(Nm\vec{b}^{\,2}/2\beta)Z(\beta) \ . \tag{13}$$

The average value of the dynamical variable $A$ is

$$\langle A\,|\,\beta,\vec{b}\rangle = \frac{a_N \int \cdots \int A\exp(-\beta\mathcal{H} - \vec{b}\cdot\vec{\mathcal{M}}) \prod_L d\vec{x}_L d\vec{p}_L}{Z(\beta,\vec{b})} \ . \tag{14}$$

The average of $\mathcal{M}_i$ is found to be

$$\langle \mathcal{M}_i\,|\,\beta,\vec{b}\rangle = -\frac{\partial\ln Z(\beta,\vec{b})}{\partial b_i} = -\frac{Nmb_i}{\beta} \ , \tag{15}$$

showing that the mean velocity is $\vec{u}=-\vec{b}/\beta$, and the average of $\mathcal{H}$ is

$$\langle \mathcal{H}\,|\,\beta,\vec{b}\rangle = -\frac{\partial\ln Z(\beta,\vec{b})}{\partial\beta} = U + \frac{Nm\vec{b}^{\,2}}{2\beta^2} \ , \tag{16}$$

where the internal energy $U$ is introduced by (8).

For abbreviation, we use $\bar{A}$ to represent the generalized canonical average $\langle A\,|\,\beta,\vec{b}\rangle$. Differentiation with respect to ensemble parameters gives the formulas

$$\partial\bar{A}/\partial\beta = -\langle \delta A\,\delta\mathcal{H}\,|\,\beta,\vec{b}\rangle \ , \tag{17a}$$

$$\partial\bar{A}/\partial b_i = -\langle \delta A\,\delta\mathcal{M}_i\,|\,\beta,\vec{b}\rangle \ . \tag{17b}$$

Equations needed in establishing the ensemble transformation in Sec. V then follow from (15)–(17):

$$\frac{\partial\bar{\mathcal{H}}}{\partial\beta} = \frac{\partial U}{\partial\beta} - \frac{Nm\vec{b}^{\,2}}{\beta^3} \ , \tag{18a}$$

$$\frac{\partial\bar{\mathcal{H}}}{\partial b_i} = \frac{\partial\bar{\mathcal{M}}_i}{\partial\beta} = \frac{Nmb_i}{\beta^2} \ , \tag{18b}$$

$$\frac{\partial \overline{\mathscr{M}}_i}{\partial b_j} = -\frac{Nm}{\beta}\delta_{ij} \; . \tag{18c}$$

The average kinetic energy now contains the translational contribution:

$$\overline{E}_{\text{kin}} = \tfrac{3}{2}NkT + \tfrac{1}{2}Nm(\vec{b}/\beta)^2 \; . \tag{19}$$

Since $\Phi$ does not depend on the atomic momenta, $\overline{\delta\Phi\delta E_{\text{kin}}}=0$, and with the aid of (17a), we find

$$\langle (\delta E_{\text{kin}})^2 \mid \beta,\vec{b}\rangle = \tfrac{3}{2}N(kT)^2 + Nm\vec{b}^{\,2}/\beta^3 \; , \tag{20}$$

$$\langle (\delta\Phi)^2 \mid \beta,\vec{b}\rangle = N(kT)^2(c-\tfrac{3}{2}) \; , \tag{21}$$

where $c$ is the constant-volume heat capacity in units of $k$ per atom:

$$c = (Nk)^{-1}(\partial U/\partial T)_V \; . \tag{22}$$

For any function that depends only on the relative atom positions and the volume, such as $\Phi$ and $\mathscr{W}$, it follows from (13) and (14) that the generalized canonical average is the same as the canonical average: $\langle \mathscr{W} \mid \beta,\vec{b}\rangle = \langle \mathscr{W} \mid \beta\rangle$. This is equivalent to the statement $\partial\overline{\mathscr{W}}/\partial b_i = 0$. This result helps in transforming expressions for thermodynamic functions, which are first obtained as canonical averages, to generalized canonical averages. For example,

$$U = \overline{\mathscr{K}} + \overline{\Phi} \; , \tag{23}$$

$$PV = -\frac{d\Omega}{d\ln V} + \tfrac{2}{3}\overline{\mathscr{K}} - \overline{\mathscr{W}} \; , \tag{24}$$

where $\mathscr{K}$ is the kinetic energy in the center-of-mass frame,

$$\mathscr{K} = (2m)^{-1}\sum_L (\vec{p}_L - m\vec{u})^2 \; , \tag{25}$$

and $\overline{\mathscr{K}} = \tfrac{3}{2}NkT$.

## IV. SUBCANONICAL ENSEMBLES

We want to construct explicitly the transformation between the molecular-dynamics and generalized canonical ensembles. It is helpful to begin with the microcanonical to canonical transformation. In addition to fixed $N$ and $V$, systems of the microcanonical ensemble are restricted to a given value $E$ of the energy. The ensemble parameter is then $E$; the weight function is $W(E) \propto \delta(\mathscr{H}-E)$, the partition function is

$$Z(E) \propto \int \cdots \int \delta(\mathscr{H}-E)\prod_L d\vec{x}_L d\vec{p}_L \; , \tag{26}$$

and the ensemble average is

$$\langle A \mid E\rangle = \frac{\int \cdots \int A\,\delta(\mathscr{H}-E)\prod_L d\vec{x}_L d\vec{p}_L}{\int \cdots \int \delta(\mathscr{H}-E)\prod_L d\vec{x}_L d\vec{p}_L} \; . \tag{27}$$

For both microcanonical and canonical ensembles the systems are in contact with linear- and angular-momentum reservoirs.[8] Hence, to construct an ordinary canonical ensemble, take a collection of microcanonical ensembles with statistical weight proportional to $e^{-\beta E}$:

$$W(\beta) \propto \int W(E)e^{-\beta E}dE \propto e^{-\beta\mathscr{H}} \; . \tag{28}$$

It follows that

$$Z(\beta) \propto \int Z(E)e^{-\beta E}dE \; , \tag{29}$$

$$\langle A \mid \beta\rangle = \frac{\int \langle A \mid E\rangle Z(E)e^{-\beta E}dE}{\int Z(E)e^{-\beta E}dE} \; . \tag{30}$$

The canonical ensemble requires $\mathscr{H} \geq -\mid G \mid$, with $\mid G \mid$ finite, which means the microcanonical functions $W(E)$, $Z(E)$, and $\langle A \mid E\rangle$ all vanish for $E < -\mid G \mid$, so the above integrals on $E$ are formally unrestricted.

In a molecular-dynamics system the atoms move according to the classical equations of motion, so within the numerical accuracy of the computation, energy and linear momentum are constants. The boundary conditions need not be specified, except that they should conserve the energy and linear momentum of the system. In general, the total angular momentum of a molecular-dynamics system fluctuates about zero; we assume this fluctuation represents the same angular-momentum reservoir as exists in the generalized canonical ensemble. Hence, there are two parameters of the molecular-dynamics ensemble: $E$ is the prescribed value of the energy, and $\vec{M}$ is the prescribed value of the linear momentum. The weight function is $W(E,\vec{M}) \propto \delta(\mathscr{H}-E)\delta(\vec{\mathscr{M}}-\vec{M})$, and the partition function and ensemble average are given, respectively, by

$$Z(E,\vec{M}) \propto \int \cdots \int \delta(\mathscr{H}-E)\delta(\vec{\mathscr{M}}-\vec{M})\prod_L d\vec{x}_L d\vec{p}_L , \tag{31}$$

$$\langle A \mid E,\vec{M}\rangle = \frac{\int \cdots \int A\,\delta(\mathscr{H}-E)\delta(\vec{\mathscr{M}}-\vec{M})\prod_L d\vec{x}_L d\vec{p}_L}{\int \cdots \int \delta(\mathscr{H}-E)\delta(\vec{\mathscr{M}}-\vec{M})\prod_L d\vec{x}_L d\vec{p}_L} \; . \tag{32}$$

To construct a generalized canonical ensemble from a collection of molecular-dynamics ensembles, introduce two parameters, $\beta$ conjugate to $\mathscr{H}$ and $\vec{b}$ conjugate to $\vec{\mathscr{M}}$:

$$W(\beta,\vec{b}) \propto \int\int W(E,\vec{M})\exp(-\beta E-\vec{b}\cdot\vec{M})dE\,d\vec{M}\,, \tag{33}$$

$$Z(\beta,\vec{b}) \propto \int\int Z(E,\vec{M})\exp(-\beta E-\vec{b}\cdot\vec{M})dE\,d\vec{M}\,, \tag{34}$$

$$\langle A \mid \beta,\vec{b}\rangle = \frac{\int\int \langle A \mid E,\vec{M}\rangle Z(E,\vec{M})\exp(-\beta E-\vec{b}\cdot\vec{M})dE\,d\vec{M}}{\int\int Z(E,\vec{M})\exp(-\beta E-\vec{b}\cdot\vec{M})dE\,d\vec{M}}\,. \tag{35}$$

Again the integrations on $E,\vec{M}$ are formally unrestricted, though the functions $W(E,\vec{M})$, etc., vanish for certain ranges of the variables.

## V. RELATIONS BETWEEN ENSEMBLE AVERAGES

With the transformation between ensembles constructed, we can now use fluctuation theory to relate different ensemble averages of the same dynamical variable. In the generalized canonical ensemble the intensive parameters are $\beta,\vec{b}$, and the average $\langle A \mid \beta,\vec{b}\rangle$ is denoted $\bar{A}$. In the molecular-dynamics ensemble the extensive variables $\mathscr{H}$ and $\mathscr{M}_i$ are held constant at the values $E$ and $M_i$, with $i=x,y,z$, and the average $\langle A \mid E=\overline{\mathscr{H}},M_i=\overline{\mathscr{M}}_i\rangle$ equals the corresponding canonical average $\bar{A}$, plus fluctuation corrections. Specifically,[9]

$$\langle A \mid \overline{\mathscr{H}},\overline{\mathscr{M}}_i\rangle = \bar{A}+\frac{1}{2}\frac{\partial}{\partial\beta}\frac{\partial\bar{A}}{\partial\overline{\mathscr{H}}} + \tfrac{1}{2}\sum_i \frac{\partial}{\partial b_i}\frac{\partial\bar{A}}{\partial\overline{\mathscr{M}}_i}+\cdots\,, \tag{36}$$

where the correction terms are of relative order $N^{-1}$ and the ellipsis represents terms of higher order. Similarly, for the ensemble averages of fluctuations,[10]

$$\langle \delta A\,\delta B \mid \overline{\mathscr{H}},\overline{\mathscr{M}}_i\rangle = \overline{\delta A\,\delta B}+\frac{\partial\bar{A}}{\partial\beta}\frac{\partial\bar{B}}{\partial\overline{\mathscr{H}}}+\sum_i \frac{\partial\bar{A}}{\partial b_i}\frac{\partial\bar{B}}{\partial\overline{\mathscr{M}}_i}+\cdots, \tag{37}$$

where the correction terms are now of relative order 1, and the ellipsis represents terms of higher order. It is useful to eliminate the extensive quantities $\overline{\mathscr{H}}$ and $\overline{\mathscr{M}}_i$ on the right sides of (36) and (37); so the correction terms can be expressed entirely in terms of the ensemble parameters $\beta$ and $b_i$. This is done by inverting Eqs. (18), and the results are

$$\langle A \mid \overline{\mathscr{H}},\overline{\mathscr{M}}_i\rangle = \bar{A}-\frac{1}{2N}\left[\mathscr{D}\frac{\beta^2}{c}\mathscr{D}\bar{A}+\frac{3\beta}{c}\mathscr{D}\bar{A} + \frac{\beta}{m}\sum_i\frac{\partial^2\bar{A}}{\partial b_i^2}\right], \tag{38}$$

$$\langle \delta A\,\delta B \mid \overline{\mathscr{H}},\overline{\mathscr{M}}_i\rangle = \overline{\delta A\,\delta B}-\frac{1}{N}\left[\frac{\beta^2}{c}(\mathscr{D}\bar{A})(\mathscr{D}\bar{B})+\frac{\beta}{m}\sum_i\frac{\partial\bar{A}}{\partial b_i}\frac{\partial\bar{B}}{\partial b_i}\right], \tag{39}$$

where $\mathscr{D}$ is the differential operator

$$\mathscr{D}=\frac{\partial}{\partial\beta}+\sum_i\frac{b_i}{\beta}\frac{\partial}{\partial b_i}\,, \tag{40}$$

and where in (39) $\mathscr{D}$ does not operate through the round brackets. These equations correct the corresponding results, Eqs. (3.4) and (3.5), of Ref. 1. Equations (38) and (39) hold for all $\beta>0$ and $\vec{b}^{\,2}\geq 0$.

As an example of the ensemble corrections, consider the total kinetic energy defined in (1). Evaluation of (38) for the molecular-dynamics average kinetic energy per atom gives

$$\frac{\langle E_{\text{kin}} \mid \overline{\mathscr{H}},\overline{\mathscr{M}}_i\rangle}{N}=\tfrac{3}{2}kT\left[1-\frac{1}{N}\left[1-\frac{3}{2c}-\frac{1}{2c}\frac{\partial\ln c}{\partial\ln T}\right]\right]+\frac{m\vec{b}^{\,2}}{2\beta^2}\,. \tag{41}$$

The last term is the kinetic energy due to the mean translational motion. The term in $N^{-1}$ expresses the fact that the molecular-dynamics average of the kinetic energy in the center-of-mass frame is not precisely the temperature. Evaluation of (39) for $(\delta E_{\text{kin}})^2$, with the aid of equations from Sec. III, gives for any value of $\vec{b}$

$$\frac{\langle (\delta E_{\text{kin}})^2 \mid \overline{\mathscr{H}},\overline{\mathscr{M}}_i\rangle}{N}=\tfrac{3}{2}(kT)^2\left[1-\frac{3}{2c}\right]. \tag{42}$$

This is the result Lebowitz *et al.*[1] obtained at $\vec{b}=0$.[11]

Concerning the pressure, the common procedure in molecular dynamics is to compute the average indicated in Eq. (24)[6,12]:

$$PV_{\text{MD}}=-\frac{d\Omega}{d\ln V}+\langle \tfrac{2}{3}\mathcal{K}-\mathcal{W}\,|\,\overline{\mathcal{H}},\overline{\mathcal{M}}_i\rangle \;. \quad (43)$$

Equation (38) gives for the ensemble correction, at any value of $\vec{b}$,

$$PV_{\text{MD}}=PV-kT\left[1-\tfrac{3}{2}\gamma+\frac{1}{2}\frac{\partial\gamma}{\partial\ln T}\right], \quad (44)$$

where $\gamma=V(\partial P/\partial U)_V$ is the Grüneisen parameter. Since $PV$ is of order $N$, the ensemble correction is of relative order $N^{-1}$. Equation (44) differs from various expressions found in the literature.[2,3,13] The difference from Lado is presumably due to the fact that Lado uses a different definition of $P$, namely, $\beta P=\partial\ln Z/\partial V$ in all ensembles, together with $\beta=\partial\ln Z/\partial E$ in all ensembles. While ensemble-dependent definitions of thermodynamic functions are legitimate as long as the definitions agree in the thermodynamic limit, the varying definitions give rise to *essential* differences in ensemble corrections and also in the mean values of fluctuations. We finally evaluate the correlated fluctuation $\delta\mathcal{W}\delta\Phi$ from Eq. (39), at any $\vec{b}$:

$$\frac{\langle\delta\mathcal{W}\delta\Phi\,|\,\overline{\mathcal{H}},\overline{\mathcal{M}}_i\rangle}{N}=\tfrac{3}{2}(kT)^2\left[\frac{1}{c}-\gamma\right]. \quad (45)$$

This again is the result obtained at $\vec{b}=0$ by Lebowitz *et al.*[1,11]

*Note added in proof.* If we use $PV=NkTf(V)$, where $f(V)$ is a function of volume, and $U=\frac{3}{2}NkT$, for hard spheres in the canonical ensemble and if we also use Eqs. (41) and (44) and observe that $E_{\text{kin}}$ and $\mathcal{K}$ are constants of the motion for hard spheres in the molecular-dynamics ensemble, then we can indeed obtain Eq. (3.27) of Ref. 2, or the equivalent Eq. (40) of Ref. 13.

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[8] In the usual definition the microcanonical ensemble is said to be composed of isolated systems; since momentum is constant for an isolated system, the quasiergodic hypothesis cannot hold under this definition of the ensemble.

[9] Equation (36) represents the next to last line of (2.10) in Ref. 1.

[10] Equation (37) represents a step between (2.11) and (2.12) in Ref. 1.

[11] That (3.7) of Ref. 1 agrees with (42) is fortuitous. Equation (3.5) of Ref. 1 will give the correct result at $\vec{b}=0$ for functions such that $\partial\bar{A}/\partial b_i=0$ and $\partial\bar{B}/\partial b_i=0$ at $\vec{b}=0$, which is the case in (3.8) of Ref. 1. Note that our $\mathcal{W}$ has the opposite sign from that of Ref. 1.

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