PHYSICAL REVIEW A VOLUME 32, NUMBER 5 NOVEMBER 1985

Laplace-transform technique for deriving thermodynamic equations from the classical microcanonical ensemble

Eric M. Pearson, Timur Halicioglu, and William A. Tiller
Department of Materials Science, Stanford University, Stanford, California 94305

(Received 12 October 1984; revised manuscript received 23 April 1985)

A new method of deriving expressions for any thermodynamic-state function as an average of the appropriate microscopic dynamical functions over the microcanonical distribution is presented. The results are valid for any system of classical particles interacting through a potential depending only on their relative positions and have a primary application to calculating thermodynamic quantities in molecular-dynamics computer-simulation studies. A Laplace-transform method is used to express any combination of energy and volume (or strain) derivatives of the microcanonical phase volume as averages of specific dynamical functions and their fluctuations. A unique result is the occurrence of the average reciprocal kinetic energy in these equations. These derivatives are then related to thermodynamic-state functions using the Legendre relations and the basic definition connecting the entropy to the phase-space volume. In particular, the complete microcanonical expressions for the adiabatic elastic constants are derived for the first time. The equations derived by this method are consistent with results from the literature pertaining to the classical microcanonical ensemble. The equivalence is obtained in the limit that the number of particles in the system approaches infinity, but the results diverge for systems with few particles. Numerical results from molecular-dynamics simulations of a simple model system are used to substantiate these points.

I. INTRODUCTION

In many texts on equilibrium statistical thermodynamics, the microcanonical ensemble is briefly introduced and then quickly abandoned in favor of the canonical, grand-canonical, and other ensembles (with several notable exceptions[1–4]). There are several reasons for this tendency. First, the mathematical formulation of the microcanonical ensemble involves the use of generalized functions (delta and step functions) which are "not convenient" for deriving statistical formulas. Second, there is some ambiguity in the basic definition of the entropy which connects the microcanonical distribution to all other thermodynamic-state functions.[5] Third, from a practical point of view, observations of real systems are rarely carried out at constant total energy. However, in recent years, computer-simulation methods have been developed which require the microcanonical formulas for their most precise interpretation. It thus becomes a practical necessity to not only have the formulas for the microcanonical ensemble available, but to also have a comprehensive theoretical technique which can be applied to new problems as they arise.

The purpose of the present paper is to discuss the following topics. In Sec. II, we present a direct and convenient method for deriving expressions which equate any thermodynamic-state function to averages of specific dynamical functions and their fluctuations over the classical microcanonical distribution. In the process, the specific expressions for a variety of thermodynamic quantities are derived. In Sec. III, we assess the effect of the various entropy definitions on our results and then compare them to previous work in the literature. In Sec. IV, we apply the derived formulas to the analysis of molecular-dynamics computer simulations.

Our entire formalism is based upon two familiar approximations in molecular and solid-state physics. The first is the Born-Oppenheimer approximation.[6] The second approximation is that the nuclear motion can be described classically, so that a system of N atoms is described by specifying the three position and momenta components of each atom, whose time evolution obeys Hamilton's equations. All of the kinetic energy of the atoms (or nuclei), including what might also be characterized in certain situations as vibrational or rotational energy, is included in the $p^2/2m$ terms. Thus we will be dealing with structureless classical particles (no internal degrees of freedom) representing atoms in any state of aggregation (molecular, liquid, solid).

The primary functions of the classical microcanonical distribution for this system are the phase-space volume $\Omega(N,V,E)$, and the phase-space density $\omega(N,V,E)$;[7–9] i.e.,

$$\Omega(N,V,E)=\frac{1}{C}\int d\mathbf{x}^1 d\mathbf{p}^1\cdots\int d\mathbf{x}^N d\mathbf{p}^N\,\Theta(E-H(\{\mathbf{x}^1,\mathbf{p}^1,\ldots,\mathbf{x}^N,\mathbf{p}^N\}))\,, \tag{1.1a}$$

$$\omega(N,V,E)=\frac{1}{C}\int d\mathbf{x}^1 d\mathbf{p}^1\cdots\int d\mathbf{x}^N d\mathbf{p}^N\,\delta(E-H(\{\mathbf{x}^1,\mathbf{p}^1,\ldots,\mathbf{x}^N,\mathbf{p}^N\}))\,, \tag{1.1b}$$

where $\Theta(\cdots)$ and $\delta(\cdots)$ are the generalized unit step and delta functions. The volume constraint is incorporated into the limits of integration over the coordinates $d\mathbf{x}^1,\ldots,d\mathbf{x}^N$ in the phase-space integrals (1.1). The microcanonical average of any dynamical function of the coordinates and momenta of the particles is then written

$$\langle A\rangle=\frac{1}{\omega C}\int d\mathbf{x}^1 d\mathbf{p}^1\cdots \times\int d\mathbf{x}^N d\mathbf{p}^N A(\{\mathbf{x}^1,\mathbf{p}^1,\ldots,\mathbf{x}^N,\mathbf{p}^N\}) \times\delta(E-H(\{\mathbf{x}^1,\mathbf{p}^1,\ldots,\mathbf{x}^N,\mathbf{p}^N\}))\ . \tag{1.2}$$

Our goal is to determine the functions $A(\{\mathbf{x}^1,\mathbf{p}^1,\ldots,\mathbf{x}^N,\mathbf{p}^N\})$ whose average over the microcanonical distribution gives any desired thermodynamic variable. The starting point is a definition for the entropy, of which there are the following two possibilities, among others:

$$S=k_B\ln\Omega\ , \tag{1.3a}$$

$$S=k_B\ln\omega\ . \tag{1.3b}$$

It has been discussed that these definitions are in agreement to order $1/N$.[5,9] We will take (1.3a) as our primary definition. In Sec. III we will show explicitly the equivalence in the $N\rightarrow\infty$ limit of using the other definition (1.3b). We will also show that our results are consistent with equations found in the literature which are derived by a method valid only in this limit.

The method outlined in Sec. II consists of two distinct tasks which convert the definitions of Eqs. (1.1)—(1.3) into the desired form. First, we use macroscopic thermodynamic equalities to write any variable as a combination of energy or volume derivatives of the entropy, pressure, or temperature. The fundamental definition (1.3a) is then employed to convert these to derivatives of the phase-space volume. The second step is the use of the Laplace-transform technique (hereafter designated LTT) to consistently evaluate the energy and volume derivatives of the phase-space volume and express them as microcanonical averages of specific dynamical functions. We then combine these results to obtain the final equations. The results for the primary microcanonical quantities—temperature, heat capacity at constant volume, pressure, stress, Grüneisen constant, and the adiabatic bulk modulus—are shown explicitly. Also shown, we believe for the first time, are the complete expressions for the adiabatic elastic constants.

The primary application of these microcanonical equations is for the analysis and interpretation of molecular-dynamics simulations,[10–12] which we will not review in any detail. Since our goal is to study the formulas we have developed and not to simulate specific materials, we have selected a simple model for the potential energy (a two-body Mie potential interaction) to perform the simulations in Sec. IV. We will provide numerical confirmation of the limits taken in Sec. III, and then compare the values for the thermodynamic derivatives against values obtained as difference derivatives over several simulations.

II. BASIC METHOD

A. Thermodynamic equalities

The thermodynamic potential whose extremum defines equilibrium at constant E and V is the entropy S. Thus any quantities which can be immediately expressed as E and V derivatives of S will be the fundamental quantities from which all other thermodynamic variables are constructed. Neglecting strain for the moment, we thus consider

$$\left[\frac{\partial S}{\partial E}\right]_V=\frac{1}{T},\quad \left[\frac{\partial T}{\partial E}\right]_V=\frac{1}{C_V},\quad \left[\frac{\partial P}{\partial E}\right]_V=\frac{\gamma}{V}\ ,$$
$$\left[\frac{\partial S}{\partial V}\right]_E=\frac{P}{T},\quad \left[\frac{\partial T}{\partial V}\right]_E=-\frac{1}{V\alpha_E},\quad \left[\frac{\partial P}{\partial V}\right]_E=-\frac{B_E}{V}\ , \tag{2.1}$$

with the usual notation of T for temperature, P for pressure, C_V for the heat capacity at constant volume, and γ for the Grüneisen parameter. The other two quantities, α_E and B_E, are defined in a manner consistent with the usual definition of the thermal expansion coefficient (α_T) and the adiabatic (B_S) or isothermal (B_T) bulk moduli. Although they are not useful thermodynamic quantities in themselves (i.e., if you heat a system, how must you change the volume to keep the internal energy constant), they will appear in the expressions for other useful quantities, and thus are retained for notational convenience.

Thermodynamic Legendre relations[13] can be used to relate any other thermodynamical variables to the basic quantities in Eq. (2.1). (See Table I.)

To formulate similar equations for stress and elastic constants, we begin with the following basic definitions:[14]

$$dE=T\,dS+V\sum_{i,j=1}^{3}\tau_{ij}\,d\eta_{ij}\ , \tag{2.2a}$$

$$\tau_{ij}=\frac{1}{V}\left[\frac{\partial E}{\partial\eta_{ij}}\right]_{S,\eta'_{\bar{i}\bar{j}}}\ , \tag{2.2b}$$

$$C^S_{ijkl}=\frac{1}{V}\left[\frac{\partial^2 E}{\partial\eta_{ij}\,\partial\eta_{kl}}\right]_{S,\eta''_{\bar{i}\bar{j},\,\bar{k}\bar{l}}}\ , \tag{2.2c}$$

where the set $\eta\equiv\{\eta_{ij},\ i,j=1,2,3\}$ are the Lagrangian strain parameters which measure the deformation from an initial reference configuration; $\eta'_{\bar{i}\bar{j}}\equiv\{\eta_{i'j'},\ i',j'=1,2,3\}\setminus\{\eta_{ij}\}$ and $\eta''_{\bar{i}\bar{j},\,\bar{k}\bar{l}}\equiv\{\eta_{i'j'},\ i',j'=1,2,3\}\setminus\{\eta_{ij},\eta_{kl}\}$. τ_{ij} are the stresses and C^S_{ijkl} are the adiabatic elastic constants. Equations (2.2b) and (2.2c) are to be evaluated in the reference configuration, that is, at zero strain. Using Eq. (2.2a), we may reexpress Eqs. (2.2b) and (2.2c) in the desired form as

$$\tau_{ij}=-\frac{T}{V}\left[\frac{\partial S}{\partial\eta_{ij}}\right]_{E,\eta'_{\bar{i}\bar{j}}}\ , \tag{2.3a}$$

TABLE I. Contributions to the expression for partial derivatives. The subscripts signify the quantity being held constant. A partial derivative is formed when the listed contribution for the thermodynamic potential is divided by that for the independent variable; e.g., contributions from $\partial P\,|_E$ and $-\partial V\,|_E$ combine to give $-(\partial P/\partial V)_E=(B_E/V)/(-1)(1)=-B_E/V$, in agreement with Eq. (2.1).

Thermodynamic potential or independent variable	Contribution to the expression	Thermodynamic potential or independent variable
$\partial E\,|_V\rightarrow$	1	$\leftarrow-\partial V\,|_E$
$\partial P\,|_V\rightarrow$	$\frac{\gamma}{V}$	$\leftarrow-\partial V\,|_P$
$\partial T\,|_V\rightarrow$	$\frac{1}{C_V}$	$\leftarrow-\partial V\,|_T$
$\partial S\,|_V\rightarrow$	$\frac{1}{T}$	$\leftarrow-\partial V\,|_S$
$\partial P\,|_E\rightarrow$	$\frac{B_E}{V}$	$\leftarrow-\partial E\,|_P$
$\partial S\,|_E\rightarrow$	$-\frac{P}{T}$	$\leftarrow-\partial E\,|_S$
$\partial T\,|_E\rightarrow$	$-\frac{1}{V\alpha_E}$	$\leftarrow-\partial E\,|_T$
$\partial P\,|_T\rightarrow$	$\frac{1}{V}\left[\frac{\gamma}{V\alpha_E}+\frac{B_E}{C_V}\right]$	$\leftarrow-\partial T\,|_P$
$\partial S\,|_T\rightarrow$	$\frac{1}{T}\left[\frac{1}{V\alpha_E}-\frac{P}{C_V}\right]$	$\leftarrow-\partial T\,|_S$
$\partial S\,|_P\rightarrow$	$-\frac{1}{VT}(B_E+\gamma P)$	$\leftarrow-\partial P\,|_S$

$$C^S_{ijkl}=-\frac{T}{V}\left[\frac{\partial^2 S}{\partial\eta_{ij}\,\partial\eta_{kl}}\right]_{E,\eta''_{\overline{ij},\overline{kl}}}-V\tau_{ij}\tau_{kl}\left[\frac{\partial^2 S}{\partial E^2}\right]_\eta -T\left[\tau_{kl}\left[\frac{\partial^2 S}{\partial\eta_{ij}\,\partial E}\right]_{\eta'_{\overline{ij}}} +\tau_{ij}\left[\frac{\partial^2 S}{\partial\eta_{kl}\,\partial E}\right]_{\eta'_{\overline{kl}}}\right]. \tag{2.3b}$$

Finally, we take the entropy definition of Eq. (1.3a) and combine it with Eqs. (2.3) and (2.1) to generate the following relations between the macroscopic variables and the phase-space volume integral and its derivatives:

$$k_BT=\frac{\Omega}{\omega}\,, \tag{2.4a}$$

$$P=\left[\frac{1}{\omega}\frac{\partial\Omega}{\partial V}\right]_{E,\eta}, \tag{2.4b}$$

$$\tau_{ij}=-\frac{1}{V}\left[\frac{1}{\omega}\frac{\partial\Omega}{\partial\eta_{ij}}\right]_{E,V,\eta'_{\overline{ij}}}, \tag{2.4c}$$

$$\frac{C_V}{Nk_B}=\left[N-Nk_BT\left[\frac{1}{\omega}\frac{\partial^2\Omega}{\partial E^2}\right]_{V,\eta}\right]^{-1}, \tag{2.4d}$$

$$\frac{\gamma}{V}=\left[\frac{1}{\omega}\frac{\partial^2\Omega}{\partial E\,\partial V}\right]_\eta-\left[\frac{1}{\omega}\frac{\partial^2\Omega}{\partial E^2}\right]_{V,\eta}\left[\frac{1}{\omega}\frac{\partial\Omega}{\partial V}\right]_{E,\eta}, \tag{2.4e}$$

$$\frac{\alpha_E}{k_B}=\left[PV-Vk_BT\left[\frac{1}{\omega}\frac{\partial^2\Omega}{\partial E\,\partial V}\right]_\eta\right]^{-1}, \tag{2.4f}$$

$$\frac{B_E}{V}=-\left[\frac{1}{\omega}\frac{\partial^2\Omega}{\partial V^2}\right]_{E,\eta}+\left[\frac{1}{\omega}\frac{\partial^2\Omega}{\partial E\,\partial V}\right]_\eta\left[\frac{1}{\omega}\frac{\partial\Omega}{\partial V}\right]_{E,\eta}, \tag{2.4g}$$

$$C^S_{ijkl}=-\frac{1}{V}\left[\frac{1}{\omega}\frac{\partial^2\Omega}{\partial\eta_{ij}\,\partial\eta_{kl}}\right]_{E,V,\eta''_{\overline{i,j}},\overline{kl}} -V\tau_{ij}\tau_{kl}\left[\frac{1}{\omega}\frac{\partial^2\Omega}{\partial E^2}\right]_{V,\eta} -\left[\tau_{kl}\left[\frac{1}{\omega}\frac{\partial^2\Omega}{\partial\eta_{ij}\,\partial E}\right]_{V,\eta'_{\overline{ij}}} +\tau_{ij}\left[\frac{1}{\omega}\frac{\partial^2\Omega}{\partial\eta_{kl}\,\partial E}\right]_{V,\eta'_{\overline{kl}}}\right]. \tag{2.4h}$$

B. Laplace-transform technique

We must now evaluate the phase-space volume derivatives appearing in Eqs. (2.4b)–(2.4h) using the definitions (1.1) and (1.2). We begin by rewriting these integrals in a more convenient form. This is accomplished by taking the Laplace transform with respect to energy, doing the momentum integrals by virtue of the separable classical Hamiltonian, and then inverse transforming to obtain the following:

$$\Omega(N,V,E)=\frac{1}{C_0\Gamma(3N/2+1)}\int d\mathbf{x}^1\cdots\int d\mathbf{x}^N[E-\Phi(\{\mathbf{x}^1,\ldots,\mathbf{x}^N\})]^{3N/2}\Theta(E-\Phi(\{\mathbf{x}^1,\ldots,\mathbf{x}^N\}))\ , \tag{2.5a}$$

$$\omega(N,V,E)=\frac{1}{C_0\Gamma(3N/2)}\int d\mathbf{x}^1\cdots\int d\mathbf{x}^N[E-\Phi(\{\mathbf{x}^1,\ldots,\mathbf{x}^N\})]^{3N/2-1}\Theta(E-\Phi(\{\mathbf{x}^1,\ldots,\mathbf{x}^N\}))\ , \tag{2.5b}$$

$$\langle A\rangle=\frac{1}{\omega C_0\Gamma(3N/2)}\int d\mathbf{x}^1\cdots\int d\mathbf{x}^N A(\{\mathbf{x}^1,\ldots,\mathbf{x}^N\})[E-\Phi(\{\mathbf{x}^1,\ldots,\mathbf{x}^N\})]^{3N/2-1}\Theta(E-\Phi(\{\mathbf{x}^1,\ldots,\mathbf{x}^N\})\ , \tag{2.5c}$$

where $\Gamma(n)$ is the gamma function, with the property that $\Gamma(n+1)=n\Gamma(n)$ and $\Gamma(1)=1$, and the new constant C_0 is given as

$$\frac{1}{C_0}=\frac{1}{C}(2\pi m)^{3N/2}\ .$$

Although the expressions (2.5) are not first given in the present work, their consistent application to the derivation of microcanonical formulas as described here is novel. Essential to these derivations is the realization that the total kinetic energy is actually a function of the coordinates in the integrals (2.5) because of the constraint on the total energy. As an important example, we write out explicitly the expression for the temperature:

$$k_BT=\frac{\Omega}{\omega}=\frac{1}{\omega C_0\Gamma(3N/2+1)}\times\int d\mathbf{x}^1\cdots\int d\mathbf{x}^N[E-\Phi(\{\mathbf{x}^1,\ldots,\mathbf{x}^N\})]^{3N/2}\times\Theta(E-\Phi(\{\mathbf{x}^1,\ldots,\mathbf{x}^N\}))\ .$$

Comparing this to Eq. (2.5c) gives immediately

$$k_BT=\frac{2}{3N}\langle E-\Phi\rangle=\frac{2}{3N}\langle K\rangle\ . \tag{2.6a}$$

This is the equipartition theorem,[15,16] but derived here in a simple way.

A more interesting example is

$$\left\{\left(\frac{\partial^2\Omega}{\partial E^2}\right)_{V,\eta}\right\}_L=s^2\{\Omega\}_L=\frac{1}{C_0}\int d\mathbf{x}^1\cdots\int d\mathbf{x}^N e^{-s\Phi(\{\mathbf{x}^1,\ldots,\mathbf{x}^N\})}\left(\frac{1}{s}\right)^{3N/2-1}$$

which can be inverse transformed to give

$$\frac{1}{\omega}\left(\frac{\partial^2\Omega}{\partial E^2}\right)_{V,\eta}=\frac{1}{\omega C_0\Gamma(3N/2-1)}\times\int d\mathbf{x}^1\cdots\int d\mathbf{x}^N[E-\Phi(\{\mathbf{x}^1,\ldots,\mathbf{x}^N\})]^{3N/2-2}\times\Theta(E-\Phi(\{\mathbf{x}^1,\ldots,\mathbf{x}^N\}))\ .$$

Comparison with (2.5c) then shows that

$$\frac{1}{\omega}\left(\frac{\partial^2\Omega}{\partial E^2}\right)_{V,\eta}=\left(\frac{3N}{2}-1\right)\langle K^{-1}\rangle\ , \tag{2.6b}$$

where $\langle K^{-1}\rangle$ is the average of the reciprocal of the kinetic energy.

The volume (or configuration) constraint has been included in the limits of integration over the coordinates. We must change variables to remove this dependence, thereby introducing a Jacobian into the integral. For the volume derivatives, we simply make the often-used transformation[17]

$$x_i=V^{1/3}x_i'\ ,\quad i=1,2,\ldots,3N$$

which introduces a Jacobian of V^N.

The results of applying the above formalism to the derivatives appearing in Eqs. (2.4) are as follows:

$$k_BT=\frac{2}{3N}\langle K\rangle\ , \tag{2.7a}$$

$$\frac{1}{\omega}\left(\frac{\partial^2\Omega}{\partial E^2}\right)_{V,\eta}=\left(\frac{3N}{2}-1\right)\langle K^{-1}\rangle\ , \tag{2.7b}$$

$$\frac{1}{\omega}\left(\frac{\partial\Omega}{\partial V}\right)_{E,\eta}=\rho k_BT-\left\langle\left(\frac{\partial\Phi}{\partial V}\right)_{E,\eta}\right\rangle\ , \tag{2.7c}$$

$$\frac{1}{\omega}\left(\frac{\partial\Omega}{\partial\eta_{ij}}\right)_{V,E,\eta'_{\overline{ij}}}=Nk_BT\delta_{ij}-\langle\Phi_{ij}\rangle\ , \tag{2.7d}$$

$$\frac{1}{\omega}\left[\frac{\partial^2\Omega}{\partial E\,\partial V}\right]_{\eta}=\rho-\left[\frac{3N}{2}-1\right]\left\langle\left[\frac{\partial\Phi}{\partial V}\right]_{E,\eta}K^{-1}\right\rangle , \tag{2.7e}$$

$$\frac{1}{\omega}\left[\frac{\partial^2\Omega}{\partial E\,\partial\eta_{ij}}\right]_{V,\eta'_{\overline{ij}}}=N\delta_{ij}-\left[\frac{3N}{2}-1\right]\langle\Phi_{ij}K^{-1}\rangle , \tag{2.7f}$$

$$\frac{1}{\omega}\left[\frac{\partial^2\Omega}{\partial V^2}\right]_{E,\eta}=\frac{N(N-1)}{V^2}k_BT-\left\langle\left[\frac{\partial^2\Phi}{\partial V^2}\right]_{E,\eta}\right\rangle-2\rho\left\langle\left[\frac{\partial\Phi}{\partial V}\right]_{E,\eta}\right\rangle+\left[\frac{3N}{2}-1\right]\left\langle\left[\frac{\partial\Phi}{\partial V}\right]^2_{E,\eta}K^{-1}\right\rangle , \tag{2.7g}$$

$$\frac{1}{\omega}\left[\frac{\partial^2\Omega}{\partial\eta_{ij}\,\partial\eta_{kl}}\right]_{E,V,\eta''_{\overline{ij},\overline{kl}}}=-Nk_BTD_{ijkl}+N^2k_BT\delta_{ij}\delta_{kl}-\langle\Phi_{ijkl}\rangle$$

$$-N(\langle\Phi_{ij}\rangle\delta_{kl}+\langle\Phi_{kl}\rangle\delta_{ij})+\left[\frac{3N}{2}-1\right]\langle\Phi_{ij}\Phi_{kl}K^{-1}\rangle . \tag{2.7h}$$

ρ $(=N/V)$, is the number density and we have used the shorthand notation

$$\Phi_{ij}=\left[\frac{\partial\Phi}{\partial\eta_{ij}}\right]_{E,V,\eta''_{\overline{ij}}} ,$$

$$\Phi_{ijkl}=\left[\frac{\partial^2\Phi}{\partial\eta_{ij}\,\partial\eta_{kl}}\right]_{E,V,\eta''_{\overline{ij},\overline{kl}}} .$$

The matrix $\underline{D}$ and the Kronecker delta δ_{ij} result from the strain derivatives of the Jacobian. In Voigt notation, the matrix is

$$\underline{D}=\begin{bmatrix}2&0&0&0&0&0\\0&2&0&0&0&0\\0&0&2&0&0&0\\0&0&0&1&0&0\\0&0&0&0&1&0\\0&0&0&0&0&1\end{bmatrix} .$$

C. Final results

The only remaining task is to combine Eqs. (2.7) with Eqs. (2.4) and collect terms into a sensible order. We list below some of the more important results:

$$k_BT=\frac{2}{3N}\langle K\rangle , \tag{2.8a}$$

$$\frac{C_V}{Nk_B}[\tfrac{2}{3}\langle K\rangle\langle K^{-1}\rangle+N(1-\langle K\rangle\langle K^{-1}\rangle)]^{-1} , \tag{2.8b}$$

$$P=\rho k_BT-\left\langle\left[\frac{\partial\Phi}{\partial V}\right]_{E,\eta}\right\rangle , \tag{2.8c}$$

$$\tau_{ij}=-\rho k_BT\delta_{ij}+\frac{1}{V}\langle\Phi_{ij}\rangle , \tag{2.8d}$$

$$\gamma=\frac{Nk_B}{C_V}+\left[\frac{3N}{2}-1\right]V\left[\left\langle\left[\frac{\partial\Phi}{\partial V}\right]_{E,\eta}\right\rangle\langle K^{-1}\rangle-\left\langle\left[\frac{\partial\Phi}{\partial V}\right]_{E,\eta}K^{-1}\right\rangle\right] , \tag{2.8e}$$

$$B_S=\rho k_BT\left[1+2\gamma-\frac{Nk_B}{C_V}\right]+V\left\langle\left[\frac{\partial^2\Phi}{\partial V^2}\right]_{E,\eta}\right\rangle$$

$$-\left[\frac{3N}{2}-1\right]V\left[\left\langle\left[\frac{\partial\Phi}{\partial V}\right]^2_{E,\eta}K^{-1}\right\rangle-2\left\langle\left[\frac{\partial\Phi}{\partial V}\right]_{E,\eta}\right\rangle\left\langle\left[\frac{\partial\Phi}{\partial V}\right]_{E,\eta}K^{-1}\right\rangle+\left\langle\left[\frac{\partial\Phi}{\partial V}\right]_{E,\eta}\right\rangle^2\langle K^{-1}\rangle\right] , \tag{2.8f}$$

$$C^S_{ijkl}=\rho k_BT\left[D_{ijkl}+\frac{Nk_B}{C_V}\delta_{ij}\delta_{kl}\right]+\frac{1}{V}\langle\Phi_{ijkl}\rangle$$

$$+\rho k_BT\left[\frac{3N}{2}-1\right][(\langle\Phi_{ij}\rangle\langle K^{-1}\rangle-\langle\Phi_{ij}K^{-1}\rangle)\delta_{kl}+(\langle\Phi_{kl}\rangle\langle K^{-1}\rangle-\langle\Phi_{kl}K^{-1}\rangle)\delta_{ij}]$$

$$+\frac{1}{V}\left[\frac{3N}{2}-1\right](\langle\Phi_{ij}\rangle\langle\Phi_{kl}K^{-1}\rangle+\langle\Phi_{kl}\rangle\langle\Phi_{ij}K^{-1}\rangle-\langle\Phi_{ij}\Phi_{kl}K^{-1}\rangle-\langle\Phi_{ij}\rangle\langle\Phi_{kl}\rangle\langle K^{-1}\rangle) . \tag{2.8g}$$

The most significant feature of these equations is the appearance of the reciprocal kinetic energy, both directly and in fluctuation terms together with the potential-energy derivatives.

III. ASYMPTOTIC LIMITS

A. Expansion of reciprocal averages

In this section, we will derive asymptotic expressions for several Eqs. (2.8) in the limit $N \to \infty$. The general approach is to make the following expansion for the average of the reciprocal kinetic energy:

$$\langle K^{-1}\rangle = \frac{1}{\langle K\rangle}\left\langle \frac{1}{1+\delta K}\right\rangle \simeq \frac{1}{\langle K\rangle}[1-\delta K+(\delta K)^2-\cdots\,] ,$$

where we have defined the normalized mean deviation

$$\delta K = \frac{K-\langle K\rangle}{\langle K\rangle} \ll 1 . \tag{3.1}$$

The condition (3.1) is always obtained in the limit $N \to \infty$. This method is easily extended to averages of the form $\langle K^{-2}\rangle$ and $\langle AK^{-1}\rangle$, where A is any other dynamical function. We will consistently retain terms to second order in the normalized mean deviation; either $(\delta K)^2$ or $(\delta K)(\delta A)$.

Applying these expansions to Eqs. (2.8b) and (2.8e)—(2.8g) yields

$$\frac{C_V^\infty}{Nk_B} = \left[\frac{2}{3} - N\left[\frac{\langle K^2\rangle - \langle K\rangle^2}{\langle K\rangle^2}\right]\right]^{-1} , \tag{3.2a}$$

$$\gamma^\infty = \frac{Nk_B}{C_V^\infty} + \frac{3NV}{2\langle K\rangle^2}\left[\left\langle \left[\frac{\partial\Phi}{\partial V}\right]_{E,\eta} K\right\rangle - \left\langle \left[\frac{\partial\Phi}{\partial V}\right]_{E,\eta}\right\rangle \langle K\rangle\right] , \tag{3.2b}$$

$$B_S^\infty = \rho k_B T\left[1+2\gamma^\infty - \frac{Nk_B}{C_V^\infty}\right] + V\left\langle \left[\frac{\partial^2\Phi}{\partial V^2}\right]_{E,\eta}\right\rangle - \frac{V}{k_B T}\left[\left\langle \left[\frac{\partial\Phi}{\partial V}\right]_{E,\eta}^2\right\rangle - \left\langle \left[\frac{\partial\Phi}{\partial V}\right]_{E,\eta}\right\rangle^2\right] , \tag{3.2c}$$

$$C_{ijkl}^{S,\infty} = \rho k_B T\left[D_{ijkl} + \frac{Nk_B}{C_V^\infty}\delta_{ij}\delta_{kl}\right] + \frac{1}{V}\langle \Phi_{ijkl}\rangle$$
$$+\frac{\rho}{\langle K\rangle}[(\langle \Phi_{ij}K\rangle - \langle \Phi_{ij}\rangle\langle K\rangle)\delta_{kl} - (\langle \Phi_{kl}K\rangle - \langle \Phi_{kl}\rangle\langle K\rangle)\delta_{ij}] - \frac{1}{Vk_B T}(\langle \Phi_{ij}\Phi_{kl}\rangle - \langle \Phi_{ij}\rangle\langle \Phi_{kl}\rangle) . \tag{3.2d}$$

B. Entropy definition

We have consistently chosen the entropy definition of (1.3a) for all equations derived in Sec. III A. This expression for the entropy can be justified by an argument based on the invariance of the phase-space volume under adiabatic changes in the external mechanical parameters which constrain the system (such as the configurational volume).[18,19] Other arguments can be made which lead to definition (1.3b).[8,20] We now present and compare the results obtained by using the LTT on definition (1.3b).

Following the method of Sec. III A, we can derive the following:

$$(k_B T)_\omega = \left[\left[\frac{3N}{2} - 1\right]\langle K^{-1}\rangle\right]^{-1} , \tag{3.3a}$$

$$\left[\frac{C_V}{Nk_B}\right]_\omega = \left[\frac{3N}{2} - 1\right]\left[N\left[\frac{3N}{2} - 1\right] - N\left[\frac{3N}{2} - 2\right]\frac{\langle K^{-2}\rangle}{\langle K^{-1}\rangle^2}\right]^{-1} , \tag{3.3b}$$

$$(P)_\omega = \frac{N}{V}(k_B T)_\omega - \left\langle \left[\left[\frac{\partial\Phi}{\partial V}\right]_{E,\eta}\right]_\omega K^{-1}\right\rangle \langle K^{-1}\rangle^{-1} . \tag{3.3c}$$

The subscript ω designates the use of the alternate entropy definition (1.3b). We now expand the reciprocal kinetic energy terms in Eqs. (3.3) to obtain their asymptotic limits. First, for the temperature,

$$(k_BT)_\omega^\infty=\frac{2\langle K\rangle}{3N}\left[\left\{1-\frac{2}{3N}\right\}\frac{\langle K^2\rangle}{\langle K\rangle^2}\right]^{-1} . \tag{3.4a}$$

The term in square brackets approaches unity as $O(1/N)$, thus $(k_BT)_\omega^\infty$ approaches Eq. (2.8a) as $O(1/N)$. For the pressure,

$$\begin{aligned}(P)_\omega^\infty={}&\rho k_BT-\left\langle\left[\left\{\frac{\partial\Phi}{\partial V}\right\}_{E,\eta}\right]_\omega\right\rangle\\&+\left\{\langle K\rangle^2\left\langle\left[\left\{\frac{\partial\Phi}{\partial V}\right\}_{E,\eta}\right]_\omega\right\rangle\right.\\&\left.-\langle K\rangle\left\langle\left[\left\{\frac{\partial\Phi}{\partial V}\right\}_{E,\eta}\right]_\omega K\right\rangle\right\}\langle K^2\rangle^{-1} .\end{aligned} \tag{3.4b}$$

If Eq. (3.4b) is to be equivalent to the previously derived pressure equation (2.8c), then the last term must approach zero in the $N\rightarrow\infty$ limit. We assume that this limit will be obtained due to the fluctuation character of this term. The validity of this assumption will be demonstrated by the numerical results of Sec. III C. Finally, for the heat capacity,

$$\begin{aligned}\left[\frac{C_V}{Nk_B}\right]_\omega^\infty={}&\left\{\frac{2}{3}-N\left[\frac{\langle K^2\rangle-\langle K\rangle^2}{\langle K\rangle^2}\right]\right.\\&\left.\times\left[\frac{\langle K\rangle^2}{\langle K^2\rangle}\left[2\frac{\langle K\rangle^2}{\langle K^2\rangle}-1\right]\right]\right\}^{-1} ,\end{aligned} \tag{3.4c}$$

The term in square brackets goes to unity as $O(1/N)$, which then yields a result equivalent to the expansion (3.2a).

We have thus shown in specific cases that the application of the LTT to the two different entropy definitions (1.3) leads to expressions which give consistent results to $O(1/N)$ as $N\rightarrow\infty$. In Sec. III C, we will see that the explicit calculation of these quantities for a model system confirms these conclusions.

C. Comparison with results from the literature

Thus far, we have developed a set of equations and their limiting forms for evaluating thermodynamic-state variables as averages of microscopic dynamical functions over the microcanonical ensemble. Some of these results, as previously indicated, are not unique to this work. However, the first work which attempted to develop a consistent method for deriving microcanonical equations for higher-order thermodynamic quantities is, to our knowledge, that of Lebowitz, Percus, and Verlet,[21] which we will hereafter refer to as LPV. In this work, they developed an expression relating the square and cross fluctuations of any dynamical functions between any two different ensembles based upon the same microscopic Hamiltonian. They then applied this general result to the derivation of formulas for the microcanonical ensemble from the canonical ensemble. Other authors have confirmed their results and extended them to derivations of additional formulas.[22,23] We will now show that the asymptotic forms of the LTT equations (3.2) are identical to the LPV equations.

We list below the expressions which result from the LPV method as given by Cheung:[23]

$$\frac{C_V}{Nk_B}=n_Q\left[1-\frac{N\langle(\delta Q)^2\rangle}{n_Qk_B^2T^2}\right]^{-1} , \tag{3.5a}$$

$$\left[\frac{\partial P}{\partial T}\right]_V=\frac{k_B}{n_Q}\left[\frac{C_V}{Nk_B}\right]\left[\rho-\frac{N\langle\delta Q\,\delta\Pi_Q\rangle}{k_B^2T^2}\right] , \tag{3.5b}$$

$$\begin{aligned}\beta_S=\frac{1}{B_S}={}&\left[\frac{2P+\rho k_BT}{3}+\frac{\rho k_BT}{n_Q}\right.\\&\left.+\langle\Xi\rangle-\frac{N\langle(\delta\Pi_Q)^2\rangle}{\rho k_BT}\right]^{-1} .\end{aligned} \tag{3.5c}$$

The Grüneisen constant can be written in terms of (3.5b) as

$$\gamma=\frac{V}{C_V}\left[\frac{\partial P}{\partial T}\right]_V=\left[\frac{1}{n_Q}-\frac{V\langle\delta Q\,\delta\Pi_Q\rangle}{n_Qk_B^2T^2}\right] . \tag{3.5d}$$

We must now convert these results into the current notation. Q is the average kinetic energy per atom, defined such that $\langle Q\rangle=\frac{3}{2}k_BT$.

The other two dynamical functions appearing in (3.5) are

$$\Pi_Q=\frac{\rho}{n_Q}Q-\frac{1}{3V}\sum_{\substack{i,j\\(i<j)}}R_{ij}\left[\frac{\partial\Phi}{\partial R_{ij}}\right]_{R'_{\overline{ij}}} , \tag{3.6a}$$

$$\Xi=\frac{1}{9V}\sum_{\substack{i,j\\(i<j)}}\sum_{\substack{k,l\\(k<l)}}R_{ij}R_{kl}\left[\frac{\partial^2\Phi}{\partial R_{ij}\,\partial R_{kl}}\right]_{R''_{\overline{ij},\overline{kl}}} . \tag{3.6b}$$

In these expressions, i,j,k,l label different particles with the summations being over all distinct pairs of particles. R_{ij} are the interparticle distances. (The sets R' and R'' and the sets η' and η'' are similarly defined.) Π_Q is called the pressure function because $\langle\Pi_Q\rangle=P$. It is a matter of some algebraic manipulation to show that

$$\Pi_Q=\frac{2}{3V}K-\frac{\partial\Phi}{\partial V} , \tag{3.7a}$$

$$\Xi=V\frac{\partial^2\Phi}{\partial V^2}+\frac{2}{3}\frac{\partial\Phi}{\partial V} . \tag{3.7b}$$

Upon inserting the relations (3.7) into Chueng's equations (3.5) and rearranging terms, the LPV equations become identical, term for term, with asymptotic limits of the LTT results (3.2). In Sec. IV, we will confirm this result using the exact numerical evaluations of both the LPV and LTT equations from the same molecular-dynamics simulation. Differences in the two methods will be discussed in the conclusions.

TABLE II. Basic simulation characteristics.

Quantity	S1	S2	S3
E/N (eV/atom)	-2.6869	-2.6870	-2.7044
Ω_0 (Å^3)	17.5136	17.5658	17.5136
$\langle T \rangle$ (K)	1060.3	1051.3	990.5
$\langle P \rangle$ (eV/atom)	0.074 54	0.012 21	0.022 95

IV. MOLECULAR-DYNAMICS SIMULATIONS

We have simulated a simple model system to numerically confirm the results of the preceding sections. We will show that the exact LTT equations (2.8) do in fact produce results which agree to $O(1/N)$ with the LPV (or asymptotic LTT) equations (3.2) and the alternate entropy equations (3.3). In addition, by performing several simulations with slightly different total energies and volumes, we have calculated difference derivatives to compare with the direct values obtained from these equations.

We chose a system of 500 particles on an fcc lattice using the usual periodic boundary conditions. A Mie potential[24]

$$\phi(r_{ij})=\frac{\epsilon}{m-n}\left[n\left[\frac{R_0}{r_{ij}}\right]^m-m\left[\frac{R_0}{r_{ij}}\right]^n\right]$$

was used with the parameters selected as $\epsilon=0.344\,66$ eV, $R_0=42.968$ Å, $m=12$, and $n=6$ (which thus becomes the Lennard-Jones 6-12 function). The atomic volume Ω_0 was selected to give near-zero pressures for the specified potential. A cutoff radius falling between the fifth and sixth neighbor shells was used. The exact value was chosen to make the direct contribution plus integral correction equal to the infinite lattice sum value for the potential. Integral corrections were then applied to all the calculated quantities as necessary.

TABLE III. Comparison of equations. (γ and C_V/Nk_B are dimensionless.)

Quantity	LTT	LPV	$S=k_B\ln\omega$
Simulation S1			
k_BT (eV)	0.091 38		0.091 45
P (eV/atom)	0.074 54		0.075 02
C_V/Nk_B	2.632 47	2.629 22	2.631 81
γ	2.649 17	2.644 70	
B_S	21.3268	21.3600	
Simulation S2			
k_BT (eV)	0.090 60		0.090 66
P (eV/atom)	0.012 21		0.012 74
C_V/Nk_B	2.958 04	2.965 98	2.946 45
γ	2.931 66	2.936 21	
B_S	20.7270	20.7569	
Simulation S3			
k_BT (eV)	0.085 36		0.085 43
P (eV/atom)	0.022 95		0.023 40
C_V/Nk_B	2.647 35	2.642 85	2.647 96
γ	2.635 68	2.631 51	
B_S	21.1945	21.2263	

The data we will present are from three simulations (S1–S3) with the basic characteristics shown in Table II. Each simulation ran for 1200 steps using a time step of 5.0×10^{-15} seconds. Averages were made over the last 1000 steps every fourth step. Increasing the averaging to every second step did not alter the results significantly. We will comment on our statistics later.

The main purpose of the computer study is to confirm the equivalence of the various equations. The simulation results are shown in Table III. The clear conclusion is that indeed all the equations are consistent. Thus, from a practical point of view, it does not matter which of the sets of equations (2.8), (3.2), or (3.3) are used.

From Table II, we see that simulations S1 and S2 are at the same energy with slightly different volumes, and vice versa for simulations S1 and S3. We can thus use the data from Table II to form difference derivative approximations to the thermodynamic quantities. The comparison between the values calculated from the above equations and those calculated directly by the LTT equations are shown in Table IV. The values for the heat capacity and Grüneisen constant are only within about 10% for simulations S1 and S3, although Table III shows that the values from simulation S2 are in much better agreement. All three simulations apparently give good numbers for the bulk modulus.

The data from Table IV taken alone do not conclusively prove that the microcanonical equations we have presented are correct in an absolute sense. The simulations need to run longer to generate adequate statistics. However, the question of statistics was discussed in the references on the LPV equations,[21,23] in which the validity of those equations was established. Our primary goal of providing a numerical confirmation of the equivalence of the various equations of the preceding sections has been achieved. We thus did not chose to commit computer resources to investigate the more costly question of the comparison to difference derivatives, especially since this has already been done for the LPV and thus, as shown here, the analytically equivalent LTT equations.

V. DISCUSSION

In Sec. II, we developed a new method, the LTT, for deriving thermodynamic equations from the classical microcanonical ensemble. First, we identified the primary statistical functions of this ensemble, the phase integrals of Eqs. (1.1) and (1.2), and related the thermodynamic-

TABLE IV. Comparison to difference derivatives. (C_V/Nk_B and γ are dimensionless.)

Quantity	Simulations	Difference derivative	Direct LTT value
C_V/Nk_B	S1		2.6325
	and	2.902	
	S3		2.6474
γ	S1		2.6492
	and	2.949	
	S3		2.6357
$V\left[\frac{\partial P}{\partial V}\right]_E$ (eV/atom)	S1		-21.1323
	and	-20.956	
	S2		-20.6908

state functions to them and their energy and volume derivatives. Second, we used the Laplace transform to convert the generalized step and delta functions in the formal representations of these phase integrals into usable forms. Finally, we consistently used Eq. (2.5) for the average of some general dynamical function to identify the specific averages involved in all other phase integrals resulting from taking the energy or volume derivatives.

In Secs. III and IV, we developed asymptotic expressions for the LTT equations and then proceeded to demonstrate their equivalence in the $N\rightarrow\infty$ limit to results obtained with a method already available in the literature. Although there is always some intrinsic merit in discovering new ways to derive and substantiate old results in statistical mechanics, we feel that there are several other reasons for considering the LTT.

The LTT demonstrates that the average reciprocal kinetic energy (as opposed to the reciprocal of the average kinetic energy) is an important dynamical quantity in the microcanonical ensemble. Indeed, higher-order energy derivatives will generate terms involving $\langle K^{-n}\rangle$ and their fluctuations. There is some intrinsic interest in the occurrence of these terms. There may also be some economy of notation, since the expansions in the $N\rightarrow\infty$ limit can be more cumbersome, especially for the higher-order energy derivatives. The LTT also provides a straightforward approach for deriving the elastic constants, which have not, as far as we know, been derived using the LPV method. In fact, it was our interest in the elastic constants which motivated this work. Higher-order volume or strain derivatives are also directly accessible by this method.

The LTT is a comprehensive method for deriving all thermodynamic quantities. The LPV method only applies to quantities containing fluctuation terms, so that other arguments must be made to define the pressure and temperature. In addition, for the LPV method, one first requires a relationship between a thermodynamic quantity and various fluctuation terms from some other ensemble, such as the canonical ensemble. For thermodynamic quantities which are fundamental to the microcanonical distribution, such as given in (2.1), the appropriate Legendre transformations into V and T derivatives, to facilitate their expression with canonical phase averages, will yield an equation with many terms. Upon applying the LPV method, many of these terms must cancel to recover the simpler microcanonical forms. We expect this to be particularly important for higher-order strain derivatives, such as the third- and fourth-order elastic constants. Use of the direct LTT method is clearly desirable in such cases.

Finally, the LTT results are ostensibly applicable to systems with a small number of particles, as indicated by the results in Secs. III and IV. However, there are some more general questions involved with this point. If one is truly interested in a small number of particles contained in an appropriately small volume, then we know that the details of the interaction at the volume boundary will play an important role in determining the behavior of the system. That is, the number of atoms in the interface region is a significant fraction of the total number of atoms, so that enforcing a volume constraint either with a fixed "wall Hamiltonian" or by limiting the region of integration in phase space is not expected to produce reasonable results. Thus, even though the LTT and the LPV method diverge for small N, the theoretical basis for both methods disappears for small N, so that the point is moot.

This then raises the question of the connection of the molecular-dynamics simulation technique with its small number of particles and its periodic boundary conditions to the actual phase space for the macroscopic system being simulated. We have seen that the LTT and the LPV method do give different numerical results to $O(1/N)$. Again, from a practical point of view, this difference will usually be eclipsed by the overall statistical accuracy limitations stemming from the finite length of the simulation. However, the formal question remains as to which equations, the LTT or the LPV, are more appropriate based upon the computational approximations of using periodic boundary conditions to model a large system with a small one. We cannot answer that question here. However, it seems certain that the theoretical tools used to attack this problem must not already contain any assumptions about the size of the system. Thus, the LTT formalism may prove useful in answering such questions.

As an example of this use of the LTT, consider the two entropy definitions (1.3) and the corresponding equations for the temperature, (2.8a) and (3.3a). The first definition yields the equipartition theorem identically, while the second only does so, as shown by (3.4a), in the $N \rightarrow \infty$ limit. This may be taken as further evidence that the definition (1.3a), $S = k_B \ln \Omega$, is the most correct definition for the entropy, even though it is unimportant for any explicit practical numerical calculations.

In summary, the LTT provides a straightforward and relatively simple method for manipulating the microcanonical ensemble. It can be used to generate the appropriate equations for analyzing molecular-dynamics computer simulations. It may also facilitate more general statements concerning the mechanics of small systems at constant energy and volume.

ACKNOWLEDGMENTS

We would like to thank the Computational Chemistry Group at NASA Ames Research Center (Grant No. NCC 2-297) for providing the computer facilities used in carrying out the numerical calculations. The remainder of this work was performed under U.S. Defense Advanced Research Projects Agency (DARPA) Contract No. MDA-903-83-K0041.

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