Fundamental treatment of the isoenthalpic-isobaric ensemble

J. R. Ray and H. W. Graben
Department of Physics and Astronomy, Clemson University, Clemson, South Carolina 29634-1911
(Received 10 February 1986)

Fluctuation formulas which are characteristic of the classical isoenthalphic-isobaric ensemble are derived in a direct and fundamental way. The technique used is adapted from a new method introduced by Pearson, Halicioglu, and Tiller [Phys. Rev. A 32, 3030 (1985)] in their treatment of the microcanonical ensemble. The application of this new method to other adiabatic ensembles is also discussed.

I. INTRODUCTION

Pearson, Halicioglu, and Tiller[1] have made a significant contribution to the classical theory of the microcanonical ensemble. For instance, they provide the simplest and most fundamental way to derive exact fluctuation formulas unique to this adiabatic ensemble.[2,3] The purpose of our paper is to further illustrate their method by applying it to another adiabatic ensemble[4] which is gaining prominence by its adaptation[5] to constant pressure molecular-dynamics simulations[6] of matter.

The basic statistical mechanics of the isoenthalpic-isobaric ensemble has already been presented by Ray, Graben, and Haile.[7] Two fluctuation formulas characteristic of this adiabatic ensemble were first derived[8] by transforming known formulas from other, isothermal ensembles. The three basic fluctuation formulas for this ensemble were derived in Ref. 7 by a method of adiabatic differentiation of certain potentials. Although this latter procedure is simple to apply, the elegant and rigorous method of Pearson *et al.*[1] (hereafter designated PHT) obviates such previously used techniques for adiabatic ensembles. We also point out in Sec. IV several other adiabatic ensembles to which the PHT method may be applied.

II. THE *HPN* ENSEMBLE

The isoenthalpic-isobaric or *HPN* ensemble consists of N identical particles adiabatically confined within a variable volume V which is maintained at a constant pressure P. Under these conditions the enthalpy H remains constant as well. The phase-space volume $\Omega(H,P,N)$ and the phase-space density $\omega(H,P,N)=(\partial\Omega/\partial H)_{P,N}$ are given by[7]

$$\Omega(H,P,N)=\frac{1}{C}\int\Theta(H-PV-\mathscr{H})d\tau\,, \tag{1}$$

$$\omega(H,P,N)=\frac{1}{C}\int\delta(H-PV-\mathscr{H})d\tau\,, \tag{2}$$

where Θ and δ are the generalized unit step and delta functions, C is a constant, $\mathscr{H}$ is the total Hamiltonian, and $d\tau$ is the elementary phase-space volume of the N particles times dV.

The adiabatically invariant form of the entropy S and the absolute temperature T, both written as functions of H, P, and N, are given by

$$S=k_B\ln\Omega\,, \tag{3}$$

$$k_BT=\Omega/\omega\,, \tag{4}$$

where k_B is Boltzmann's constant.

We now consider the class of particle Hamiltonians in which the potential energy Φ is a function of spatial coordinates only. The momenta enter as quadratic terms in the kinetic energy K, and integration[9] over these coordinates can be carried out in Eq. (1). This calculation produces the volume of a $3N$-dimensional sphere whose radius squared is equal to $2m(H-PV-\Phi)$, where m is the single-particle mass. These considerations reduce Eqs. (1) and (2) to the forms

$$\Omega(H,P,N)=\frac{1}{C_0\Gamma(3N/2+1)}\times\int(H-PV-\Phi)^{3N/2}\Theta(H-PV-\Phi)d\tau'\,, \tag{5}$$

$$\omega(H,P,N)=\frac{1}{C_0\Gamma(3N/2)}\times\int(H-PV-\Phi)^{3N/2-1}\Theta(H-PV-\Phi)d\tau'\,, \tag{6}$$

where $C_0=C/(2\pi m)^{3N/2}$, Γ is the standard gamma function, and $d\tau'$ is the elementary spatial volume of the N particles times dV. Note that Eq. (5) can be obtained directly from Eq. (1) without recourse to Laplace transforms, and that Eq. (6) is generated from Eq. (5) by $\omega=(\partial\Omega/\partial H)_{P,N}$.

Following similar lines the ensemble average of any dynamical function of the spatial coordinates q and volume, $A(q,V)$, is given by

$$\langle A\rangle=\frac{1}{\omega C_0\Gamma(3N/2)}\times\int A(H-PV-\Phi)^{3N/2-1}\Theta(H-PV-\Phi)d\tau'\,. \tag{7}$$

PHT made the simple, but apparently theretofore overlooked observation that the total dynamic kinetic energy, which is a function of the particle momenta, can be expressed in terms of spatial coordinates only (under conditions of constant energy and volume) through the trivial equation $K=E-\Phi$! The extension of this idea to the present ensemble yields

$$K=H-PV-\Phi\ . \tag{8}$$

That is, for constant H and P (and N) the kinetic energy is expressible in terms of the volume V and the spatial coordinates of the particles through Φ. Upon inserting K for A in Eq. (7) and using Eqs. (5), (6), and (4), we obtain the fundamental connection between kinetic energy and temperature

$$\langle K\rangle=(3N/2)k_BT\ . \tag{9}$$

III. FUNDAMENTAL FLUCTUATIONS

In this section new derivatives are given of the fluctuation formulas containing the isobaric heat capacity C_P, adiabatic compressibility κ_S, and isobaric volume expansivity α_P. These calculations in the *HPN* ensemble serve to further illustrate the power and simplicity of the PHT method as well as to verify previous results.

First, we introduce the thermodynamic definitions

$$C_P=(\partial H/\partial T)_P\ , \tag{10}$$

$$\begin{aligned}V\kappa_S&=-(\partial V/\partial P)_S\\&=-(\partial V/\partial P)_H-V(\partial V/\partial H)_P\ ,\end{aligned} \tag{11}$$

$$\begin{aligned}V\alpha_P&=(\partial V/\partial T)_P\\&=-(\partial S/\partial P)_H+(\partial S/\partial H)_P(\partial T/\partial P)_H(\partial H/\partial T)_P\ ,\end{aligned} \tag{12}$$

where the subscript N on all partial derivatives has been suppressed. The corresponding expressions in the *HPN* ensemble are

$$k_B/C_P=[\partial(\Omega/\omega)/\partial H]_P\ , \tag{13}$$

$$\langle V\rangle\kappa_S=-(\partial\langle V\rangle/\partial P)_H-\langle V\rangle(\partial\langle V\rangle/\partial H)_P\ , \tag{14}$$

$$\langle V\rangle\alpha_P=-(k_B/\Omega)\times\left[(\partial\Omega/\partial P)_H-\left[\frac{(\partial\Omega/\partial H)_P(\partial\langle K\rangle/\partial P)_H}{(\partial\langle K\rangle/\partial H)_P}\right]\right]. \tag{15}$$

Using Eqs. (5), (6), and (7), we obtain in a straightforward way the exact results:

$$k_B/C_P=1-(1-2/3N)\langle K\rangle\langle K^{-1}\rangle\ , \tag{16}$$

$$\langle V\rangle\kappa_S=(3N/2-1)(\langle V^2K^{-1}\rangle-2\langle V\rangle\langle VK^{-1}\rangle+\langle V\rangle^2\langle K^{-1}\rangle)\ , \tag{17}$$

$$\langle V\rangle\alpha_P/C_P=(3N/2)(\langle VK^{-1}\rangle-\langle V\rangle\langle K^{-1}\rangle)\ . \tag{18}$$

To derive asymptotic expressions for the foregoing quantities in the limit $N\to\infty$, we make use of the expansion

$$\langle K^{-1}\rangle=\langle K\rangle^{-1}\langle 1-\delta K+(\delta K)^2\cdots\rangle\ , \tag{19}$$

where $\delta K=(K-\langle K\rangle)/\langle K\rangle\ll 1$. The results are

$$C_P^\infty/Nk_B=[\tfrac{2}{3}-N\langle(\delta K)^2\rangle]^{-1}\ , \tag{20}$$

$$k_BT\kappa_S^\infty=\langle V\rangle\langle(\delta V)^2\rangle\ , \tag{21}$$

$$k_BT\alpha_P^\infty/C_P^\infty=-\langle\delta(KV)\rangle\ , \tag{22}$$

where

$$\langle\delta(KV)\rangle=(\langle KV\rangle-\langle K\rangle\langle V\rangle)/(\langle K\rangle\langle V\rangle)\ .$$

Equations (20) and (21) were derived in Ref. 8 by transforming known fluctuation equations over to the *HPN* ensemble, whereas Eqs. (20), (21), and (22) were derived in Ref. 7 by adiabatic differentiation of certain thermodynamic potentials. The use of the PHT procedure, as presented in this section, gives a simple and clear derivation of these same results and also confirms their validity.

IV. DISCUSSIONS

As seen in the previous section the PHT methods can be applied to the *HPN* ensemble to give an improved derivation of the fluctuation formulas for this ensemble. An extension of the *HPN* ensemble which has proven useful for treating solids is the isoenthalpic-isotension or *HtN* ensemble.[10] Here t is the thermodynamic tension tensor. The *HtN* ensemble is an adiabatic ensemble and fluctuation formulas for the adiabatic elastic constants, the thermal expansion tensor at constant tension, and the specific heat at constant tension were derived in Ref. 11. Also presented in Ref. 11 were fluctuation formulas for the higher-order elastic constants. Using the PHT method we could produce an improved derivation of these same results.

A counterpart to the *HtN* ensemble is a microcanonical ensemble in which the size and shape of the system is held constant. If the matrix h specifies the shape and size of the system then we are discussing the *EhN* ensemble. This ensemble was given a detailed treatment in Ref.10 where fluctuation formulas were presented for the adiabatic elastic constants, the temperature coefficients of thermodynamic tension, and the isostrain specific heat. The fluctuation formulas have been tested in recent molecular dynamics calculations[12] where it was shown that they furnish a very efficient and convenient method for calculating elastic constants and other thermodynamic properties of solids. PHT have rederived the fluctuation formulas for the adiabatic elastic constants in this ensemble using their elegant method.

Note that Eqs. (16), (17), and (18) are exact results for the (*HPN*) ensemble based on the entropy definition of Eq. (3). Such exact results contain the reciprocal kinetic energy in the ensemble averages. However, in their asymptotic forms, Eqs. (20), (21), and (22), this is not the case, and these formulas, which may be obtained by

transformation theory or adiabatic differentiation of potentials, are verified and given a more complete derivation.

In the method of differentiation of potentials one first constructs a new potential whose adiabatic differentiation leads to the relevant fluctuation formula; we refer the reader to Refs. (3), (7), and (11) for examples of the use of this method. In the Appendix we show how the PHT procedure can be used to justify the basic equations of this method of deriving fluctuation formulas.

In summary, PHT have discovered an important calculational method which may be used to derive various predictions and properties of adiabatic ensembles. It is a curious fact that their important and simple method has lain undiscovered until this time.

APPENDIX

References 3 and 7 present direct derivations of the primary fluctuation formulas in the microcanonical ensemble and in the *HPN* ensemble, whereas Refs. 10 and 11 contain such derivations in the *EnH* and $H+N$ ensembles. Each derivation begins by choosing (with foresight) a newly defined potential. Here, we would like to consider one such potential to illustrate the relationship between this earlier method and that of PHT.

Let us choose Eq. (7) of Ref. 3 as our starting point. Casting the equation in current notation gives

$$Y=\frac{1}{C}\int K\Theta(E-\mathscr{H})d\tau\ ,$$

where $d\tau$ is the elementary $6N$-dimensional phase-space volume of microcanonical ensemble theory. Upon integrating over the momenta, we find

$$\begin{aligned} Y&=\omega\langle K^2\rangle/(3N/2+1)\\ &=[(3N/2)/(3N/2+1)]\langle K^2\rangle\Omega/\langle K\rangle\\ &=\{[1+\langle(\delta K)^2\rangle]/(1+2/3N)\}\langle K\rangle\Omega\ . \end{aligned}$$

The asymptotic form ($N\rightarrow\infty$) is

$$Y^{\infty}=\langle K\rangle\Omega\ .$$

Thus, Eq. (10) of Ref. 3 is rigorously justified.

[1]E. M. Pearson, T. Halicioglu, and W. A. Tiller, Phys. Rev. A **32**, 3030 (1985).
[2]J. L. Lebowitz, J. K. Percus, and L. Verlet, Phys. Rev. **153**, 250 (1967); P. S. Y. Cheung, Mol. Phys. **33**, 519 (1977).
[3]J. R. Ray and H. W. Graben, Mol. Phys. **43**, 1293 (1981).
[4]W. B. Brown, Mol. Phys. **1**, 68 (1958).
[5]H. C. Anderson, J. Chem. Phys. **72**, 2384 (1980).
[6]J. M. Haile and H. W. Graben, J. Chem. Phys. **73**, 2412 (1980).
[7]J. R. Ray, H. W. Graben, and J. M. Haile, Nuovo Cimento **64B**, 191 (1981).
[8]J. M. Haile and H. W. Graben, Mol. Phys. **40**, 1433 (1980).
[9]A. Münster, *Statistical Thermodynamics* (Springer, Berlin, 1969), Vol. I, Chap. 1.
[10]J. R. Ray and A. Rahman, J. Chem. Phys. **80**, 4423 (1984).
[11]J. R. Ray, J. Appl. Phys. **53**, 6441 (1982).
[12]J. R. Ray, M. C. Moody, and A. Rahman, Phys. Rev. B **32**, 733 (1985); **33**, 895 (1986).