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Ensemble Dependence of Fluctuations with Application to Machine Computations*

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The standard theory of fluctuations in thermodynamic variables in various ensembles is generalized to nonthermodynamic variables: e.g., the mean-square fluctuations of the kinetic energy K in a classical microcanonical ensemble at fixed energy E is given, for large systems, by $\langle(\delta K)^2\rangle/\langle K\rangle = T[1-3/2C)$, where T is the temperature (corresponding to the energy E) and C is the specific heat per particle (in units of Boltzmann's constant). The general results may be expressed in terms of the asymptotic behavior of the Ursell functions in various ensembles. Applications are made to molecular dynamic computations where time averages correspond (via ergodicity) to phase averages in an ensemble with fixed energy and momentum. The results are also useful for time-dependent correlations.

I. INTRODUCTION

It is generally believed (and partially proven[1]) that all thermodynamic properties of a physical system may be computed from any of the various Γ-space ensembles, e.g., canonical, grand-canonical, microcanonical, constant-total-momentum, isobaric, etc., commonly used in statistical mechanics. The reason for this is that in the thermodynamic limit (size of system → ∞) appropriate to the various ensembles, the expected values of phase functions corresponding to "intensive" or per-unit-volume (per particle) properties of the system are independent of the ensemble used. Care must be exercised, of course, in the region of thermodynamic singularities, i.e., at phase transitions, and we shall not discuss the relevant extensions here.

The kinetic energy per particle

$$k=\frac{K}{N}=\frac{1}{N}\sum_{i=1}^{N} p_i^2/2m \tag{1.1}$$

is an example of such an intensive property. Its value may be computed in a canonical ensemble (c.e.) with fixed reciprocal temperature β, particle number N, and volume Ω, it may also be computed in a microcanonical ensemble (m.e.) at fixed N, Ω, and energy per particle

$$\epsilon=H/N=K/N+\Phi/N,$$

where

$$\Phi=\tfrac{1}{2}\sum{}' \varphi(q_i-q_j) \tag{1.2}$$

is the potential energy. The results differ only by terms $o(N)$ as $N\to\infty$, with $\rho=N/\Omega$ kept fixed.[2] That is, separating explicitly the fixed parameters,

$$\langle k(Q^N,P^N)\,|\,\beta,\rho,N\rangle=\langle k(Q^N,P^N)\,|\,\bar{\epsilon},\rho,N\rangle+o(N), \tag{1.3}$$

where Q^N, P^N denote the full system phase space of coordinates and momenta $(q_1,\cdots q_N,\, p_1,\cdots p_N)$, and

$$\bar{\epsilon}=\bar{\epsilon}(\beta,\rho,N)\equiv\langle H(Q^N,P^N)/N\,|\,\beta,\rho,N\rangle \tag{1.4}$$

is given the value obtained from the canonical ensemble. Here the volume Ω is fixed by rigid or periodic boundary conditions, the precise nature of which is unimportant to our considerations.

An equation similar to (1.3) holds for the virial

$$\langle \mathcal{W}(Q^N,P^N)\rangle\equiv\left\langle\sum_i\left[\frac{1}{3m}p_i^2+\tfrac{1}{6}\sum_j(\mathbf{q}_i-\mathbf{q}_j)\cdot\frac{\partial\varphi(\mathbf{q}_i-\mathbf{q}_j)}{\partial\mathbf{q}_i}\right]\right\rangle$$
$$\equiv\langle\mathcal{W}_K+\mathcal{W}_\Phi\rangle=NP/\rho, \tag{1.5}$$

where P is the pressure. In general, we expect an ensemble-independent average in the thermodynamic limit for the value per particle of a function A of the form

$$A(\mathbf{Q}^N,\mathbf{P}^N)=\sum_{i=1}^{N} a(\mathbf{q}_i,\mathbf{p}_i;\,\mathbf{Q}^N,\mathbf{P}^N),$$

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[1] See, e.g., M. E. Fisher, Arch. Ratl. Mech. Anal. 17, 377 (1964); R. Griffith, J. Math. Phys. 6, 1447 (1965). J. Van der Linden, Physica 32, 642 (1966).

[2] Explicit forms for the $o(N)$ terms are given in J. L. Lebowitz and J. K. Percus, Phys. Rev. 124, 1673 (1961) and references quoted therein. Some of these have been used and verified explicitly in machine computations with 1000 particles by J. L. Anderson, J. K. Percus, and J. Steadman (to be published).

where

$$a(\mathbf{q}_i,\mathbf{p}_i;\,\mathbf{Q}^N,\mathbf{P}^N)=\sum_{j_1\cdots j_n} a(\mathbf{q}_i,\mathbf{p}_i;\,\mathbf{q}_{j_1},\mathbf{p}_{j_1},\cdots\mathbf{q}_{j_n},\mathbf{p}_{j_n}),\quad(1.6)$$

and

$$a(\mathbf{q}_i,\mathbf{p}_i;\,\mathbf{q}_{j_1}\cdots\mathbf{p}_{j_n})\rightarrow 0\quad\text{when}\quad|\mathbf{q}_i-\mathbf{q}_{j_s}|\rightarrow\infty\,.$$

Here n is independent of N, and a vanishes sufficiently strongly at ∞ so that the integral over the $\mathbf{q}_{j_s}$ exists. For large enough systems, we can then use any convenient ensemble to compute expectation values of quantities like A.

The situation is quite different, however, when we consider fluctuations. Let us define

$$L_{\alpha\gamma}=\langle A_\alpha A_\gamma\rangle-\langle A_\alpha\rangle\langle A_\gamma\rangle\qquad(1.7)$$

in any ensemble, for quantities of the form (1.6). Then in the thermodynamic limit (in a single phase system), we expect

$$\lim_{\langle N\rangle\to\infty}\left[\frac{1}{\langle N\rangle}L_{\alpha\gamma}\right]=l_{\alpha\gamma}\qquad(1.8)$$

to exist, where we have used $\langle N\rangle$ instead of N to include the possibility of a grand ensemble. The quantity $l_{\alpha\gamma}$ will however *not* be independent of the ensemble. For example, if $A_\alpha=A_\gamma=H$, then $l_{\alpha\gamma}=0$ in the m.e. but is proportional to the specific heat per particle in the c.e. In comparing classical-canonical with grand-canonical ensemble expectations, the momentum distributions are identical. The relation between fluctuations in functions of the coordinates is then obtainable from the asymptotic properties of the spatial distribution $n_{s+t}(\mathbf{q}_1,\cdots\mathbf{q}_{s+t})$ when the set of s particles is far removed from the set of t particles. Indeed, it has been shown that[3]

$$\text{g.c.e.:}\quad n_{s+t}(z)\rightarrow n_s(z)n_t(z)\,,\qquad(1.9)$$

$$\text{c.e.:}\quad n_{s+t}(N)\rightarrow n_s(N)n_t(N)-\frac{\rho T}{N}\chi\left(\rho\frac{\partial n_s(N)}{\partial\rho}\right)\times\left(\rho\frac{\partial n_t(N)}{\partial\rho}\right),\qquad(1.10)$$

in the grand-canonical and canonical ensemble, respectively, where χ is the isothermal compressibility. It is our purpose here to obtain a general and useful relation between fluctuations in different ensembles. (Our analysis here will be restricted to classical systems, the generalization to quantum systems may involve problems of commutation relations.)

II. EXPECTATIONS UNDER TRANSFORMATIONS OF ENSEMBLE

Suppose that we know the expected value of a quantity $A(\mathbf{R})$, where $\mathbf{R}$ denotes a point of the full phase space, in an ensemble specified by extensive variables V_1, V_2, $\cdots$, as well as by parameters which will not be specified since they will not be altered. Hence

$$\langle A\,|\,V_1,V_2,\cdots\rangle=\int W(\mathbf{R}\,|\,V_1,V_2,\cdots)A(\mathbf{R})d\mathbf{R}/W(V_1,V_2\cdots),\qquad(2.1)$$

where $W(\mathbf{R}|\,V_1,V_2\cdots)$ is the appropriate statistical weight and

$$W(V_1,V_2,\cdots)=\int W(\mathbf{R}\,|\,V_1,V_2\cdots)d\mathbf{R}=e^{-\Psi(V_1,V_2\cdots)}\qquad(2.2)$$

the associated partition function, with the property that in the thermodynamic limit,

$$\lim_{\langle N\rangle\to\infty}\frac{1}{\langle N\rangle}\Psi(V_1,V_2\cdots)=\psi(v_1,v_2\cdots)\qquad(2.3)$$

exists, with $v_i=V_i/\langle N\rangle$. A Legendre transformation to intensive variables X_1, $X_2\cdots$ now results from the definition

$$W(\mathbf{R}\,|\,X_1,X_2,\cdots)=\int\cdots\int W(\mathbf{R}\,|\,V_1,V_2\cdots)\times\exp[-\sum X_iV_i]d\mathbf{V},\qquad(2.4)$$

so that

$$e^{-\Psi(X_1,X_2\cdots)}=\int\cdots\int e^{-[\Psi(V_1,V_2\cdots)+\Sigma X_iV_i]}d\mathbf{V},\qquad(2.5)$$

and

$$\langle A\,|\,X_1,X_2\cdots\rangle=e^{\Psi(X_1,X_2\cdots)}\int\cdots\int\langle A\,|\,V_1,V_2,\cdots\rangle\times\exp-[\Psi(V_1.V_2\cdots)+\sum X_iV_i]d\mathbf{V}.\qquad(2.6)$$

In particular, we have from (2.5) and (2.6) the basic expectations and fluctuations[4] ($\bar{V}_i\equiv\langle V_i\rangle$, $\delta V_i\equiv V_i-\bar{V}_i$)

$$\bar{V}_i(X_1,X_2,\cdots)=-\partial\Psi(X_1,X_2\cdots)/\partial X_i\,,\qquad(2.7)$$

$$\langle\delta V_i\delta V_j\,|\,X_1,X_2,\cdots\rangle=\partial^2\Psi(X_1,X_2\cdots)/\partial X_i\partial X_j=-\partial\bar{V}_i/\partial X_j=-\partial\bar{V}_j/\partial X_i.\qquad(2.8)$$

In the thermodynamic limit, the exponent $\Psi(\mathbf{V})+\sum X_iV_i$ in (2.5) and (2.6) goes to infinity as $\langle N\rangle$, so that the distribution in V space, in units of $\langle N\rangle$, becomes infinitely sharp. Hence by a steepest descent expansion, or any equivalent technique,[3,5] $\langle A\,|\,\mathbf{X}\rangle$ will be given at finite $\langle N\rangle$ by $\langle A\,|\,\langle\mathbf{V}(\mathbf{X})\rangle\rangle$ plus a correction series in ascending powers of $\langle N\rangle^{-1}$. The series is most directly obtained by a Taylor expansion about the

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[3] J. L. Lebowitz and J. K. Percus, Phys. Rev. **122**, 1673 (1961); see also A. Meeron and Siegart, J. Math. Phys. **7**, 741 (1966); Z. Salsburg, J. Chem. Phys. **44**, 3090 (1966), where extensive use is made of these relations.

[4] See, e.g., L. D. Landau and E. M. Lifshitz, *Statistical Physics* (Addison-Wesley Publishing Company, Reading, Massachusetts, 1958).

[5] G. Horwitz, J. Math. Phys. (to be published).

limiting form:

$$\langle A|\mathbf{V}\rangle=\langle A|\langle\mathbf{V}(\mathbf{X})\rangle\rangle+\sum\delta V_i(\partial/\partial\bar{V}_i)\langle A|\langle\mathbf{V}(\mathbf{X})\rangle\rangle$$
$$+\tfrac{1}{2}\sum\delta V_i\delta V_j(\partial^2/\partial\bar{V}_i\partial\bar{V}_j)\langle A|\langle\mathbf{V}(\mathbf{X})\rangle\rangle+\cdots,$$

followed by an average defined by (2.6):

$$\langle A|\mathbf{X}\rangle=\langle A|\langle\mathbf{V}\rangle\rangle+\tfrac{1}{2}\sum\langle\delta V_i\delta V_j|\mathbf{X}\rangle\frac{\partial^2\langle A|\langle\mathbf{V}\rangle\rangle}{\partial\bar{V}_i\partial\bar{V}_j}+O(\langle A\rangle/\langle N\rangle). \quad (2.9)$$

Since numerical computations are simplest in a **V** ensemble while analytical computations are simpler in an **X** ensemble, (2.9) is more useful in its inverse form, now reading

$$\langle A|\langle\mathbf{V}\rangle\rangle=\langle A|X\rangle-\tfrac{1}{2}\sum\langle\delta V_i\delta V_j|\mathbf{X}\rangle\frac{\partial^2\langle A|\mathbf{X}\rangle}{\partial V_i\partial V_j}+O(\langle A\rangle/\langle N\rangle)$$
$$=\langle A|\mathbf{X}\rangle+\tfrac{1}{2}\sum\frac{\partial V_i}{\partial X_j}\frac{\partial^2\langle A|\mathbf{X}\rangle}{\partial V_i\partial V_j}$$
$$=\langle A|\mathbf{X}\rangle+\tfrac{1}{2}\sum\frac{\partial}{\partial X_j}\frac{\partial}{\partial V_j}\langle A|\mathbf{X}\rangle$$
$$=\langle A|\mathbf{X}\rangle+\tfrac{1}{2}\sum\frac{\partial}{\partial X_j}\frac{\partial X_i}{\partial V_j}\frac{\partial}{\partial X_i}\langle A|\mathbf{X}\rangle, \quad (2.10)$$

where $\mathbf{X}=\mathbf{X}(\mathbf{V})$ is the inverse function to $\langle\mathbf{V}(\mathbf{X})\rangle$. Applying (2.10) to AB, we have as well the transformation formula for fluctuations:

$$\langle\delta A\delta B|\mathbf{V}\rangle=\langle AB|\mathbf{V}\rangle-\langle A|V\rangle\langle B|\mathbf{V}\rangle$$
$$=\langle\delta A\delta B|\mathbf{X}\rangle-\sum\langle\delta V_1\delta V_j|\mathbf{X}\rangle\times\left(\frac{\partial\langle A|\mathbf{X}\rangle}{\partial V_i}\right)\left(\frac{\partial\langle B|\mathbf{X}\rangle}{\partial V_j}\right) \quad (2.11)$$
$$=\langle\delta A\delta B|\mathbf{X}\rangle+\sum\frac{\partial X_i}{\partial V_j}\frac{\partial\langle A|\mathbf{X}\rangle}{\partial X_i}\frac{\partial\langle B|\mathbf{X}\rangle}{\partial X_j}, \quad (2.12)$$

now to relative order $O(1)$. The generalization of these results to transformations between ensembles with mixed intensive and extensive variables, e.g., isobaric and grand canonical, is straightforward. [Equation (2.11) can also be derived, formally at least, by considering generalized ensembles in which the functions A and B play the role of additional $\mathbf{V}_i$'s with respect to which the ensembles are always canonical, using thermodynamic fluctuation theory and then setting the corresponding $\mathbf{X}_i$'s equal to zero.]

We note here that the functions $A(R)$ and $B(R)$ could also depend on the time t. In particular, transport coefficients can be expressed, via the Kubo relations, as expectations of fluctuations in quantities like $A(R_t)$ and $B(R)$, where R_t is the point in phase space at which R arrives after a time t. Since $\langle A(R_t)\rangle=\langle A(R)\rangle$, the relation between $\langle\delta A(R_t)\delta B(R)\rangle$ in different ensembles is independent of t and (2.11) then yields a general relation between expressions for transport coefficients in different ensembles.[6]

Asymptotic Form of the Correlation Functions

A particularly useful application of the general formalism is to the distribution and Ursell functions in the various ensembles. This leads to a generalization of (1.10) from which the relation between fluctuations in different ensembles may be found. Letting $y_i=(q_i,p_i)$, we have for any ensemble[7]

$$n_s(z_1,\cdots,z_s)=\langle\sum i_{1\neq\cdots\neq i_s}\,\delta(y_{i_1}-z_1)\cdots\delta(y_{i_s}-z_s)\rangle, \quad (2.13)$$

which is of the form (1.6) for a given set of z_i's, the n_s now being, however, $O(1)$ rather than $O\langle(N\rangle)$. Application of (2.10) then shows at once that, with obvious notation,

$$n_s(\mathbf{V})-n_s(\mathbf{X})=\tfrac{1}{2}(\partial/\partial\mathbf{X})(\partial/\partial\mathbf{V})n_s(\mathbf{X}). \quad (2.14)$$

Equation (2.14) directly implies (2.10) as $\langle A\rangle$ may be generally written as an integral over the n_s.

Further, if we introduce the generating functional

$$n[f]\equiv\sum\frac{1}{s'}\int n_s(\mathbf{y}_1,\cdots,\mathbf{y}_s)f(\mathbf{y}_1)\cdots f(y_s)d\mathbf{y}_1\cdots d\mathbf{y}_s, \quad (2.15)$$

then

$$n[f|V]=n[f|\mathbf{X}]+\tfrac{1}{2}(\partial/\partial\mathbf{X})(\partial/\partial\mathbf{V})n[f|\mathbf{X}].$$

But then to the same order in $\langle N\rangle$, the generating functional for the Ursell distribution[7] $F_s(y_1,\cdots y_s)$, where

$$F_1(y_1)=n(y_1),\ F_2(y_1,y_2)=n_2(y_1,y_2)-n_1(y_1)n_1(y_2),\ \cdots \quad (2.16)$$

has the form

$$F[f|\mathbf{V}]=\ln n[f|\mathbf{V}]=\ln n[f|\mathbf{X}]+\frac{1}{2}\frac{1}{n[f|\mathbf{X}]}\frac{\partial}{\partial\mathbf{X}}\cdot\frac{\partial}{\partial\mathbf{V}}n[f|\mathbf{X}] \quad (2.17)$$

or

$$F[f|\mathbf{V}]-F[f|\mathbf{X}]=\frac{1}{2}\frac{\partial}{\partial\mathbf{X}}\cdot\frac{\partial}{\partial\mathbf{V}}F[f|\mathbf{X}]+\frac{1}{2}\frac{\partial}{\partial\mathbf{X}}F[f|\mathbf{X}]\cdot\frac{\partial}{\partial\mathbf{V}}F[f|\mathbf{X}]. \quad (2.18)$$

If the intensive ensemble is a grand ensemble and we are considering the limit as a set of s particles diverge

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[6] See, e.g., M. S. Green, Phys. Rev. **119**, 829 (1960); R. Zwanzig, Ann. Rev. Phys. Chem. **16**, 67 (1965) for review and references.

[7] J. L. Lebowitz and J. K. Percus, J. Math. Phys. **4**, 1495 (1963).

from a set of t particles, then it is known that[3]

$$F_{s+t} \longrightarrow 0. \qquad (2.19)$$

It follows then from (2.18) that

$$F_{s+t}(\mathbf{V}) \longrightarrow \frac{1}{2}\frac{\partial}{\partial \mathbf{V}} F_s(\mathbf{X}) \cdot \frac{\partial \mathbf{V}}{\partial \mathbf{X}} \cdot \frac{\partial}{\partial \mathbf{V}} F_t(\mathbf{X}), \qquad (2.20)$$

which is a generalization of (1.10).

It should be noted that n_s and F_s are quantities $O(1)$, so that the right sides of (2.14) and (2.18) are $O(\langle N\rangle^{-1})$. These corrections are therefore important only when used in finding the expectations of quantities like fluctuations which involve integrations over the volume of the system without any "cutoff." When that happens, the first term on the right of (2.18) will give a contribution of $O(1)$, while the second term will be of $O(\langle N\rangle)$ recovering the general form (2.11).

III. FLUCTUATIONS IN MOLECULAR DYNAMIC COMPUTATIONS

In molecular dynamics calculations on high-speed digital computers,[8–10] the nature of the system parameters is quite rigidly fixed. The calculations are done by setting initial conditions for several hundred particles interacting via some pair potential and restricted to a box with periodic boundaries, and then solving the classical equations of motion. Waiting a certain amount of time for the system to "thermalize," time averages of quantities like A_α or fluctuations are then computed:

$$\langle A_\alpha \rangle_t = \frac{1}{T}\int_{t_0}^{t_0+T} A_\alpha(\mathbf{Q}^N(t),\mathbf{P}^N(t))dt, \qquad (3.1)$$

$$\bar{L}_{\alpha\gamma} = \langle A_\alpha A_\gamma \rangle_t - \langle A_\alpha \rangle_t \langle A_\gamma \rangle_t .$$

Assuming the system to be ergodic, these time averages will coincide with ensemble averages at fixed values of any of the uniform constants of the motion which exist. Consequently, the system is specified by extensive parameters: total energy $H=E$, total momentum $\mathbf{M}$, total particle number N, total volume Ω.

Let us now compare this microcanonical ensemble of molecular dynamics computations with the corresponding canonical ensemble at fixed reciprocal temperature β, center-of-mass velocity $\mathbf{v}$. Total volume Ω and particle number N are fixed in both. We shall suppose that the system is maintained at $\mathbf{M}=0$, so that $\mathbf{v}=0$ as well. Now for the canonical ensemble,

$$\begin{aligned}\langle (\delta H)^2 \rangle &= -\partial\langle H\rangle/\partial\beta = N\beta^{-2}C \\ &= N\beta^{-2}(C_K + C^i), \qquad (3.2)\end{aligned}$$

where $C_K = \frac{3}{2}$ is the kinetic component of the specific heat per particle, in units of Boltzmann's constant k, and C^i is the potential component. Further, at $\mathbf{v}=0$,

$$\begin{aligned}\langle \delta H \delta M_i \rangle &= -\partial \langle \mathbf{M} \rangle_t / \partial\beta = 0, \\ \langle (\delta M)^2 \rangle &= \langle \mathbf{M} \rangle^2 = 3N/\beta = -\partial\langle \mathbf{M} \rangle / \partial \mathbf{v}\beta. \qquad (3.3)\end{aligned}$$

Equations (2.10) and (2.11) now become

$$\begin{aligned}\langle A \,|\, E, \mathbf{M}=0 \rangle = \langle A \,|\, \beta, \mathbf{v}=0 \rangle &- \frac{1}{2}\frac{\partial}{\partial\beta}\frac{\beta^2}{NC}\frac{\partial}{\partial\beta} \\ \times \langle A \,|\, \beta, \mathbf{v}=0 \rangle &- \frac{1}{2}\frac{\partial}{\partial\mathbf{v}}\frac{1}{3N\beta}\cdot\frac{\partial}{\partial\mathbf{v}} \\ &\times \langle A \,|\, \beta, \mathbf{v} \rangle \big|_{\mathbf{v}=0}, \qquad (3.4)\end{aligned}$$

$$\begin{aligned}\langle \delta A \delta B \,|\, E, \mathbf{M}=0 \rangle = \langle \delta A \delta B \,|\, \beta, \mathbf{v}=0 \rangle &- \frac{\beta^2}{NC}\frac{\langle A \rangle_t}{\partial\beta}\frac{\langle B \rangle_t}{\partial\beta} \\ &- \frac{1}{3N\beta}\frac{\langle A \rangle_t}{\partial\mathbf{v}}\cdot\frac{\langle B \rangle_t}{\partial\mathbf{v}}\bigg|_{\mathbf{v}=0}. \qquad (3.5)\end{aligned}$$

We shall now use (3.5) to obtain theoretical values for the fluctuations $\langle (\delta K)^2 \rangle$ and $\langle \delta W \delta\Phi \rangle$ defined in (1.1) and (1.5), which were "experimentally" measured by Verlet[10] and Rahman.[9]

$$\langle (\delta K)^2 \,|\, \beta, \mathbf{v}=0 \rangle = -(\partial/\partial\beta)\langle K \rangle = 3N/2\beta^2, \qquad (3.6)$$

so that from (3.4),

$$\begin{aligned}\frac{1}{N}\langle (\delta K)^2 \,|\, E, \mathbf{M}=0 \rangle &= \frac{3}{2\beta^2}\left(1 - \frac{3}{2C}\right) \\ &= \frac{1}{N}\langle (\delta\Phi)^2 \,|\, E, \mathbf{M}=0 \rangle. \qquad (3.7)\end{aligned}$$

In other words, the kinetic-energy fluctuation is a direct measure of the specific heat, and of course, since $K+\Phi$ is constant, this is identical with the potential-energy fluctuation. Similarly, $\partial\mathcal{W}/\partial\mathbf{v}=0$ at $\mathbf{v}=0$ by parity and we find

$$\begin{aligned}&N^{-1}\langle \delta\mathcal{W}_\Phi \delta\Phi \,|\, E, \mathbf{M}=0 \rangle \\ &\quad = -N^{-1}\langle \delta\mathcal{W}_\Phi \delta K \,|\, E, \mathbf{M}=0 \rangle \\ &\quad = N^{-1}\langle \delta\mathcal{W}_\Phi \delta\Phi \,|\, \beta, \mathbf{v}=0 \rangle + N^{-1}\left(\frac{\partial\beta}{\partial E}\right)\frac{\partial\langle \mathcal{W}_\Phi \rangle}{\partial\beta}\frac{\partial\langle\Phi\rangle}{\partial\beta} \\ &\quad = (3T^2/2C)(\partial/\partial T)[(P/\rho) - T], \qquad (3.8)\end{aligned}$$

where use has been made of the relation $(\partial/\partial\beta)\langle \mathcal{W} \,|\, \beta \rangle = -\langle \delta\mathcal{W}\delta H \,|\, \beta \rangle$.

Application to Computer "Experiments"

The specific heat can be computed, using (3.7), from either the kinetic-energy or the potential-energy fluctuations, which are theoretically equal in a machine computation, where the equations of motion are inte-

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[8] B. J. Alder and T. E. Wainwright, J. Chem. Phys. **33**, 1439 (1960).

[9] A. Rahman, Phys. Rev. **136**, A405 (1964).

[10] L. Verlet, Phys. Rev. (to be published).

TABLE I. Interaction part C^i of the specific heat per atom, in units of the Boltzmann constant. (1): numerical differentiation of the internal energy. (2): calculated value using (3.9) with the results (1) in the right-hand side. (3): direct calculation of C^i using (3.9).

$\rho\sigma^3$	T/ϵ	(1) C^i	(2) C^i	(3) C^i
0.85	2.89	0.73	0.63	0.59
	2.20	0.79	0.78	0.78
	1.21	0.95	0.89	0.84
	1.13	0.99	0.86	0.78
	0.88	1.11	1.19	1.24
0.75	2.84	0.56	0.495	0.47
	0.827	0.88	0.885	0.89
0.45	4.62	0.20	0.23	0.25
	2.93	0.26	0.23	0.22
	1.71	0.28	0.42	0.46
	1.51	0.28	0.30	0.31

grated at constant density. This is only approximately so in the calculations performed by one of us,[10] some of the results of which will be given now as examples of the preceding considerations; there, the integration algorithm determines the positions at various times. The velocities are then calculated by a numerical differentiation which introduces a small apparent fluctuation of the total energy. Numerically, however, this effect is very small: The fluctuations in potential and kinetic energy differ by less than 1% when the time averages are performed on 1200 time steps of 10^{-14} sec each, using a system of 864 particles simulating argon molecules with the help of a Lennard-Jones potential $\varphi(r)=4\epsilon[(\sigma/r)^{12}-(\sigma/r)^6]$. From (3.6), we can write for the part C^i of the specific heat due to the interaction

$$\begin{aligned} C^i &= C-\tfrac{3}{2} \\ &= (\beta^2/N)\tfrac{2}{3}C(\langle\Phi^2\rangle-\langle\Phi\rangle^2). \end{aligned} \tag{3.9}$$

In Table I [column labeled (1)] are given some values of C^i, deduced from numerical differentiation of the interaction part of the internal energy with respect to the temperature along the three isochores, for which the particle density is of 0.85, 0.75, and 0.4 in units σ^{-3}. The precision is of the order of 5%. The error on the fluctuation of the potential energy is much larger, as may be seen from Table I. In the column labeled (2) are given the values obtained when, in the right-hand side of (3.8), C has been replaced by the value (1), obtained by numerical differentiation of the internal energy. In the last column are given the values of C^i derived entirely from (3.9). Although the values obtained from the first procedure—which was used to display a more direct test of (3.9)—are somewhat better, it is seen that the statistical errors are rather large and may reach 20%. On the other hand, the results are sufficiently precise to illustrate the use of (3.9) to calculate the specific heat in the microcanonical ensemble. The agreement with experiment is certainly good for the isochore at $\rho\sigma^3=0.45$, where the experimental data of Levelt[11] and the internal energy calculated from molecular dynamics agree very well. For the two high-density isotherms, we know that the equation of state $(P/\rho kT)$ derived from the molecular dynamics computations agree very well with experiment. No direct comparison is possible for the internal energies. Some experimental data are available at temperatures and densities rather near some of the points of Table I:

TABLE II. $\rho^{-1}\partial P/\partial T-1$. (1) numerical differentiation of the equation of state. (2) calculated value using (3.8).

$\rho\sigma^3$	T/ϵ	(1) $\left(\dfrac{1}{\rho}\dfrac{\partial P}{\partial T}-1\right)$	(2) $\left(\dfrac{1}{\rho}\dfrac{\partial P}{\partial T}-1\right)$
0.85	2.89	4.3	3.3
	2.20	4.4	4.0
	1.21	4.9	4.6
	1.13	5.0	4.8
	0.88	6.0	6.4
0.75	2.84	3.4	3.0
	0.827	4.9	4.7

For $\rho\sigma^3=0.84$, $(T/\epsilon)=0.836$, the experimental value is $C^i=1.07$, which should be compared with the value 1.11 at $\rho\sigma^3=0.85$, $T/\epsilon=0.88$; for $\rho\sigma^3=0.798$, $T/\epsilon=0.92$, $C^i=0.96$ experimentally; at $\rho\sigma^3=0.75$, $T/\epsilon=0.827$, $C^i=0.88$, from the molecular dynamics computation. The results are in reasonable agreement.

Also, a comparison can be made with the data which can be extracted from Rahman's work[9]; for about 800 steps of 10^{-14} sec, at $T/\epsilon=0.79$, $\rho\sigma^3=0.82$, the value $C^i=0.81$ can be derived from the temperature fluctuation given by Rahman.

The same kind of analysis can be made using the fluctuation of the product of the virial and the potential energy [Eq. (3.8)]. As above, we compare the results derived, using the formula where C has been obtained from the computed internal energy, with the results we get by differentiating the equation of state [column labeled (2) in Table II, precision around 5%]. Again, the statistical error on the fluctuation is larger, but the over-all agreement is satisfactory. The agreement with experiment is also good in view of the fact that the equation of state obtained from computation fits very well with the argon data.

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[11] J. M. H. Levelt, Physica 26, 361 (1960).