PHYSICAL REVIEW A VOLUME 31, NUMBER 2 FEBRUARY 1985

Fluctuation of thermodynamic parameters in different ensembles

Karl W. Kratky
Institut für Experimentalphysik der Universität Wien, Boltzmanngasse 5, A-1090 Wien, Austria
(Received 5 June 1984)

The relation between different thermodynamic ensembles is studied, the finiteness of the systems being explicitly taken into account. Especially, equilibrium fluctuations of thermodynamic parameters (temperature, pressure, chemical potential) are considered. Several discrepancies occur in the literature. Interpreting the pressure in a concrete way makes it possible to evaluate the solutions proposed in the literature. These considerations are then applied to the special case of computer experiments.

I. INTRODUCTION

The statistical physics of small thermodynamic systems is not as well developed as that of macroscopic systems. There is no unique solution when generalizing thermodynamic formulas to small systems.[1] Accordingly, the literature is divergent. For instance, we consider a small system in thermal contact with a macroscopic reservoir. Does the temperature of the small system fluctuate in the course of time? The answer may be yes[2] or no.[1] Also, the opinion that this question is senseless can be found.[3] The meaning of pressure in small systems is controversial.[4–6] In the present paper, various opinions occurring in the literature are compared. It is is investigated how several discrepancies can be removed and if there exists a *best* solution. In any case, phase transitions and critical points are not considered. Thus, the difference between macroscopic systems and the thermodynamic limit can be neglected throughout the paper. Furthermore, equilibrium is considered only, i.e., no systems compatible with a given ensemble are excluded.

For a start, we consider a *macroscopic isolated system* with particle number N, energy E, and volume V. One kind of particle is considered only. The entropy $S_m(N,E,V)=Ns(E/N,V/N)$ of the corresponding *microcanonical ensemble* satisfies the differential relation

$$dS_m=\alpha\, dN+\beta\, dE+\gamma\, dV\ , \tag{1a}$$

$$\alpha=-\frac{\mu}{T}=\left[\frac{\partial S_m}{\partial N}\right]_{E,V},\quad \beta=\frac{1}{T}=\left[\frac{\partial S_m}{\partial E}\right]_{N,V}, \tag{1b}$$

$$\gamma=\frac{P}{T}=\left[\frac{\partial S_m}{\partial V}\right]_{N,E},\quad P=\frac{\gamma}{\beta}=-\left[\frac{\partial E}{\partial V}\right]_{N,S_m}. \tag{1c}$$

Boltzmann's constant is set equal to unity. It is shown in the literature[7] that μ, T, and P have the usual meaning of chemical potential, absolute temperature and pressure, respectively. N, E, and V are *extensive parameters* which are also called *mechanical.*[3] α, β, and γ are *thermodynamic parameters.* As indicated previously, macroscopic systems may be characterized in the following way: The dependence of the entropy per particle on the system size (and on the ensemble) can be neglected, $s_m(N,E,V)=s(E/N,V/N)$. This means that S_m is extensive, s and the thermodynamic parameters are intensive. If deviations from this simple behavior cannot be neglected, the particular system is termed a *small system.*

The extensive parameters play different roles in a quantum-mechanical macroscopic system. The volume (including its shape) is regarded as boundary condition for the N-particle system. The volume may change continuously, the particle number not in a strict sense, but for a macroscopic system it may be treated as a continuous parameter, cf. (1). The solution of the Schrödinger equation yields eigenstates i with energy E_i. These states are per definition nondegenerate. They are very dense for a macroscopic system so that a smooth probability density $\Omega(N,E,V)$ in energy space may be defined. Then the statistical definition of entropy is [1]

$$S_m(N,E,V)=\ln\Omega(N,E,V) \tag{2}$$

for the microcanonical ensemble. Thus, the entropy corresponds to the density of states and is *no property of a single state.* First of all, the same is true for its derivatives α, β, and γ. For instance, the temperature $T=\beta^{-1}$ is a property of the whole (N,E,V) ensemble. One may think that the temperature of a single system makes no sense.[3] On the other hand, one may associate the ensemble temperature with each system of the microcanonical ensemble.[7]

II. VARIOUS ENSEMBLES OF SMALL SYSTEMS

Now we turn to small systems; however, they should not be very small, i.e., it is again possible to treat N and E as continuous variables. For an isolated system it is usually postulated[1] or argued[8] that relations (1) and (2) are still valid. This may be interpreted as a definition of α, β, and γ in small systems, the mechanical parameters (MP) being held fixed. For this microcanonical ensemble, the thermodynamic parameters (TP) are also fixed then, and no parameters fluctuate at all. Local fluctuations (e.g., density fluctuations) are not considered in this paper.

If the small system is in contact with a macroscopic reservoir, other ensembles result. The total system is again isolated, and the contact between the two subsystems is thought to be arbitrarily small. Thus, the small system may be regarded as a member of a microcanonical ensemble, but each system with different MP. In the picture of time evolution, the small system is changing its MP very slowly, at any time being in internal equilibrium. If only energy contact is allowed, this results in the *canonical ensemble* with probability density p_c in energy space[7]

$$p_c(N,E,V)=\Omega(N,E,V)\exp(-\beta_r E)/Q_c \; , \tag{3a}$$

$$Q_c \equiv \int_0^\infty dE\, \Omega(N,E,V)\exp(-\beta_r E) \tag{3b}$$

for the small system. The additive constant occurring in energy E is fixed in such a way that $E \geq 0$ in any case.[1] β_r refers to the sharp temperature of the macroscopic reservoir. N and V are fixed. Since the energy distribution is well defined, cf. (3), this is also the case for the average of E and its fluctuation. The canonical ensemble can thus be characterized in two ways:

$$(N,\beta_r,V) \text{ or } (N,\langle E \rangle,V) \; . \tag{4}$$

If particle exchange between the system and the reservoir is also allowed, it follows that

$$p_g(N,E,V)=\Omega(N,E,V)\exp(-\alpha_r N-\beta_r E)/Q_g \; , \tag{5a}$$

$$Q_g \equiv \int_0^\infty dN \int_0^\infty dE\, \Omega(N,E,V)\exp(-\alpha_r N-\beta_r E) \tag{5b}$$

for the corresponding *grand canonical ensemble.* N and E fluctuate in a well-defined way, only V being held fixed. Thus the grand canonical ensemble can be characterized by

$$(\alpha_r,\beta_r,V) \text{ or } (\langle N \rangle,\langle E \rangle,V) \; . \tag{6}$$

Volume exchange (movable piston) instead of particle exchange results in the *pressure ensemble:*

$$p_p(N,E,V)=\Omega(N,E,V)\exp(-\beta_r E-\gamma_r V)/Q_p \; , \tag{7a}$$

$$Q_p \equiv \int_0^\infty dE \int_0^\infty dV\, \Omega(N,E,V)\exp(-\beta_r E-\gamma_r V) \; , \tag{7b}$$

the pressure ensemble being characterized by

$$(N,\beta_r,\gamma_r) \text{ or } (N,\langle E \rangle,\langle V \rangle) \; . \tag{8}$$

For completeness, the corresponding relations are also stated for the *microcanonical ensemble:*

$$p_m(N,E,V)=1 \; , \tag{9a}$$

$$Q_m \equiv \Omega(N,E,V) \; , \tag{9b}$$

the microcanonical ensemble being characterized by

$$(N,E,V) \; . \tag{10}$$

The integrals $Q_m=Q_m(N,E,V)$, $Q_c=Q_c(N,\beta_r,V)$, $Q_g=Q_g(\alpha_r,\beta_r,V)$, and $Q_p=Q_p(N,\beta_r,\gamma_r)$ are called *partition functions* of the corresponding ensembles. Other ensembles are usually not considered since it is difficult to imagine ensembles where N and/or V fluctuate but E remains fixed. If all MP are allowed to fluctuate, divergences occur.[1]

As can be seen from Eqs. (4), (6), (8), and (10), any ensemble considered may be characterized by the MP of the corresponding small system. If representation in terms of fixed parameters is preferred, the fluctuating MP have to be replaced by the *conjugate* TP of the reservoir. Up to now, only the distribution of MP has been treated. To proceed to the TP, we consider the entropy again. The statistical definition of entropy S_i in ensemble i $(i=m,c,g,p)$ is given by[7]

$$S_i \equiv \langle \ln(\Omega/p_i) \rangle_i \; , \tag{11}$$

where the angular brackets refer to an average over the probability function p_i. The explicit result for the various ensembles is

$$S_m=\ln\Omega=\ln Q_m \; , \tag{12a}$$

$$S_c=\int dE\, p_c \ln(\Omega/p_c)=\ln Q_c+\beta_r\langle E \rangle_c \; , \tag{12b}$$

$$\begin{aligned} S_g&=\int dN \int dE\, p_g \ln(\Omega/p_g) \\ &=\ln Q_g+\beta_r\langle E \rangle_g+\alpha_r\langle N \rangle_g \; , \end{aligned} \tag{12c}$$

$$\begin{aligned} S_p&=\int dE \int dV\, p_p \ln(\Omega/p_p) \\ &=\ln Q_p+\beta_r\langle E \rangle_p+\gamma_r\langle V \rangle_p \; . \end{aligned} \tag{12d}$$

For simplicity, the angular brackets in (12b)—(12d) will be left out in the following. Using this notation, the entropy S_i may be expressed in terms of N_i, E_i, and V_i in any ensemble, cf. (4), (6), (8), and (10). Then, the TP are defined by[7]

$$dS_i=\alpha_i\, dN_i+\beta_i\, dE_i+\gamma_i\, dV_i \; , \tag{13}$$

a generalization of (1a) for small systems in the ensemble i. Inserting (12) yields the simple result that a TP has the same value as the corresponding parameter of the reservoir if the conjugate MP is allowed to fluctuate:

$$\begin{aligned} &\alpha_i=\alpha_r\colon\; i=g \; , \\ &\beta_i=\beta_r\colon\; i=c,g,p \; , \\ &\gamma_i=\gamma_r\colon\; i=p \; . \end{aligned} \tag{14}$$

Incidentally, the ensemble theory may be introduced in a thoroughly other way.[9] There, from an informational theoretical concept of entropy in any ensemble, probability density p_i and entropy S_i come out automatically with α_r, β_r, γ_r as formal Lagrangian parameters. The identification with thermodynamic quantities is the result of a second step only.

III. MASSIEU-PLANCK FUNCTIONS

Apart from the entropy, other thermodynamic functions are often considered. They are defined as Legendre transforms of entropy:

$$M_i^m \equiv S_i \; , \tag{15a}$$

$$M_i^c \equiv -\beta_i F_i=S_i-\beta_i E_i \; , \tag{15b}$$

$$M_i^g \equiv -\beta_i J_i=S_i-\beta_i E_i-\alpha_i N_i \; , \tag{15c}$$

$$M_i^p \equiv -\beta_i G_i=S_i-\beta_i E_i-\gamma_i V_i \; . \tag{15d}$$

F_i (free energy), J_i, and G_i are the well-known thermodynamic potentials, expressed in ensemble i. However, the more appropriate Massieu-Planck functions[1] M_i^j will be used in the following. The differential relations are

$$dM_i^m = \alpha_i \, dN_i + \beta_i \, dE_i + \gamma_i \, dV_i \ , \tag{16a}$$

$$dM_i^c = \alpha_i \, dN_i - E_i \, d\beta_i + \gamma_i \, dV_i \ , \tag{16b}$$

$$dM_i^g = -N_i \, d\alpha_i - E_i \, d\beta_i + \gamma_i \, dV_i \ , \tag{16c}$$

$$dM_i^p = \alpha_i \, dN_i - E_i \, d\beta_i - V_i \, d\gamma_i \ , \tag{16d}$$

cf. (13) and (15). For example, the independent variables of M_i^c are N_i, β_i, and V_i. Since N, β, and V are the *natural variables* for the canonical ensemble, the corresponding Massieu-Planck function is characterized by the superscript c, and so forth.

It is easy to express M_i^i in terms of partition functions Q_i. Combining (12) and (15), it follows that

$$M_i^i = \ln Q_i \ . \tag{17}$$

This simple relationship is here a consequence of the definition of entropy S_i. In Ref. 1, $M_i^i = \ln Q_i$ is introduced as a basic postulate. M_i^i is the *natural* Massieu-Planck function in ensemble i, the other M_i^j being obtained by relations (15). $Q_i = \exp(M_i^i)$, $i \neq m$, are Laplace transforms of Q_m, while M_i^j are Legendre transforms of M_i^i. The dissimilarity between these types of transformation induces that a specific Massieu-Planck function is different in different ensembles.[1] This "inconsistency"[6] is the reason for other approaches sometimes found in the literature, see also Sec. VI.

There is a *further problem* when expressing the Massieu-Planck functions in terms of Q_i. The Q_i should be dimensionless so that $\ln Q_i$ can be formed. However, only Q_c and Q_g have this property, whereas Q_m has the dimension (E^{-1}) and Q_p the dimension (V). Since only differentials $d \ln Q_i = Q_i^{-1} dQ_i$ are of physical interest, this problem seems to be a formal one.[1] However, there are also physical implications: In the microcanonical ensemble, the approximation of continuous E leads to the preceding discrepancy, see also Sec. V. In the pressure ensemble, there is even a deeper problem.[10] Volume V formally comes in as a boundary condition when solving the Schrödinger equation, while in reality, walls and pistons are also made of molecules which should be included in the Schrödinger equation. This is not so evident when the walls remain fixed. In the pressure ensemble, they are explicitly not fixed (volume exchange), so that the move of a piston between the small system and the reservoir should be taken into account. This has been done in the Born-Oppenheimer approximation[10] with the result

$$M_p^p(\text{corrected}) = \ln(Q_p \gamma_r) \ . \tag{18}$$

$(Q_p \gamma_r)$ is dimensionless, the differential $dM_p^p(\text{corrected})$ remains unchanged compared with the uncorrected Massieu-Planck function.

IV. FLUCTUATION OF THERMODYNAMIC PARAMETERS

As mentioned in Sec. II, the MP as well as the TP are fixed in the microcanonical ensemble. As to the other ensembles, at least one MP, i.e., the energy, fluctuates. Energy E varies from system to system in ensemble i, $E_i = \langle E \rangle_i$. Are similar considerations possible for the TP? *Three different opinions can be found in the literature:*

(a) The TP are properties of the whole ensemble. It is senseless to speak of any fluctuation since no TP can be associated with a single system.[3]

(b) Those TP conjugate to fluctuating MP are fixed, the others fluctuate.[1]

(c) All TP fluctuate.[2,11]

As already mentioned, the extension of statistical physics to small systems is not unique, and it seems that it cannot be decided if (a), (b), or (c) is the *best* extension, to say nothing of *truth*. We will postpone this question. Now, it will be displayed in which sense fluctuations of TP may be imagined. For simplicity, we stick to the *canonical ensemble*. $N_c = N$ and $V_c = V$ are fixed, energy E varies from system to system in the ensemble. A given system with (N_c, E, V_c) is thought to belong to a microcanonical ensemble with the same MP, cf. Sec. II. Then, the TP of the system are defined by

$$\alpha \equiv \partial \ln \Omega(N_c, E, V_c) / \partial N_c \ , \tag{19a}$$

$$\beta \equiv \partial \ln \Omega(N_c, E, V_c) / \partial E \ , \tag{19b}$$

$$\gamma \equiv \partial \ln \Omega(N_c, E, V_c) / \partial V_c \ , \tag{19c}$$

cf. (1) and (2). The average over the canonical ensemble is given by[7]

$$\langle \alpha \rangle_c = \int dE \, \alpha p_c = \partial \ln Q_c(N_c, \beta_r, V_c) / \partial N_c \ , \tag{20a}$$

$$\langle \beta \rangle_c = \int dE \, \beta p_c = \beta_r \ , \tag{20b}$$

$$\langle \gamma \rangle_c = \int dE \, \gamma p_c = \partial \ln Q_c(N_c, \beta_r, V_c) / \partial V_c \ , \tag{20c}$$

cf. (3). However, these considerations are refused by literature (a) and only accepted for α and γ by literature (b), β_c assumed to be fixed since it is conjugate to the fluctuating E, $\beta_c = \beta_r$. To illuminate the situation, we consider the differential of M_c^c, Eq. (16b):

$$dM_c^c = \alpha_c \, dN_c - E_c \, d\beta_c + \gamma_c \, dV_c \ . \tag{21a}$$

Bearing in mind that $M_c^c = \ln Q_c$, Eqs. (3) and (17), one can alternatively express the differential as

$$dM_c^c = \langle \alpha \rangle_c \, dN_c - \langle E \rangle_c \, d\beta_r + \langle \gamma \rangle_c \, dV_c \ , \tag{21b}$$

where (20a) and (20c) have been used. $\langle E \rangle_c = E_c$ and $\beta_c = \beta_r$ are already known. The interesting relations $\langle \alpha \rangle_c = \alpha_c$ and $\langle \gamma \rangle_c = \gamma_c$ come out *by chance* from the point of view of (a). According to (b), they are a hint for the reality of fluctuating α and γ, in contrast to β, which only occurs as β_r in (21b). Literature (c), however, sticks to the fact that $\langle \beta \rangle_c = \beta_r$ is equally valid, cf. (20b), so that there is no reason why to refuse a fluctuating β. However,

$$\langle T \rangle_c = \langle \beta^{-1} \rangle_c \neq \beta_r^{-1} = T_r \ . \tag{22}$$

Thus in the frame of (c) the mean temperature does not correspond to T_r.

A confusing result can be found in Ref. 7. There, it is considered to be *consistent with statistical physics* that all

TP fluctuate. Indeed, possible fluctuations of β in the canonical ensemble are treated there, but β turns out to be infinitely sharp. The solution of this paradox is simple: In the derivation of the result, a property of Ω has been used which is only valid in the thermodynamic limit.

The generalization to other ensembles i is obvious. In (c), a system belonging to ensemble i is associated with the TP via the actual MP, cf. (19). In (b), this association is restricted to TP which are conjugate to fixed MP. For the TP $\mathcal{T}$ allowed to fluctuate, it follows that

$$\langle \mathcal{T} \rangle_i = \mathcal{T}_i \; . \tag{23}$$

The corresponding *fluctuation formulas* for the TP are given in Ref. 1. They are valid for (b) and (c). For (c), additional fluctuation formulas have to be added.[2,11]

As far as the TP are considered in a formal way, the discussion about fluctuating TP remains *abstract,* and no decision can be made between the opinions (a), (b), and (c). However, the relation $P=\gamma/\beta$, Eq. (1c), provides a link between the TP and the pressure, a quantity which has a *concrete* meaning. If we think of an *isolated system* in a box, P can be calculated from the mean force exerted on the walls. In the sense of (a), (b), and (c), P has to be regarded as fixed quantity then. Now we turn to the fluctuation of γ and of P in the *canonical ensemble.* In view of (b), β is fixed. Thus,

$$\frac{\langle \gamma^2 \rangle_c - \langle \gamma \rangle_c^2}{\langle \gamma \rangle_c^2} = \frac{\langle P^2 \rangle_c - \langle P \rangle_c^2}{\langle P \rangle_c^2} \; . \tag{24}$$

In view of (c), β is allowed to fluctuate, and Eq. (24) is not valid in general. For a classical ideal gas, the left-hand side is zero.[1,4] The result for the right-hand side, however, is $2/(3N)$, see Ref. 1. This has been obtained combining two facts. For an ideal gas, the pressure is strictly proportional to the energy, and the relative fluctuation of energy is $2/(3N)$. Thus, (b) is not self-consistent if the word *pressure* is taken literally and not only formally. As to (a), no inconsistency occurs if the pressure is thought to be fixed as well as the TP. However, this would be a strange feature of pressure. We consider again a system in the canonical ensemble. In the picture of time evolution, the energy changes very slowly. Correspondingly, one could measure (via finite time averages) slow changes in pressure. If P is by definition fixed, it is considered in a formal way only. Thus, interpreting the pressure in a concrete way favors (c).

V. ALTERNATIVE APPROACH

The concrete interpretation of pressure led to the conclusion that the TP are fixed in the microcanonical ensemble, but fluctuate in the other ensembles *according to the fluctuation of the MP.* Thus the behavior of TP in any ensemble i, $i \neq m$, can be traced back to the microcanonical ensemble m. The roundabout way via entropies S_i or Massieu-Planck functions M_i^j is no longer necessary. Only the basic relations for the microcanonical ensemble, Eqs. (1) and (2), have to be considered further together with the probability functions p_i, Sec. II. However, the definition of S_m, Eq. (2), is not yet thoroughly satisfactory: $S_m = \ln\Omega$ cannot be the whole truth since Ω is not dimensionless, cf. Sec. III. This can be taken into account by defining S_m^{Δ}:

$$S_m^{\Delta} \equiv \ln(\Omega\, \Delta E) \; , \tag{25}$$

with an arbitrary but constant ΔE, yields the same derivatives as $S_m = \ln\Omega$. It is natural to interpret ΔE as the uncertainty of energy in the microcanonical ensemble.[12] Then, $\Omega\,\Delta E$ is the number of states between $E-\frac{1}{2}\Delta E$ and $E+\frac{1}{2}\Delta E$,

$$\Omega\,\Delta E = \Upsilon(N,E+\tfrac{1}{2}\Delta E) - \Upsilon(N,E-\tfrac{1}{2}\Delta E) \; , \tag{26}$$

$\Upsilon(N,E,V)$ being the number of independent solutions of the Schrödinger equation up to energy E. Statistical physics makes sense if ΔE has the following properties:

(i) There are enough states within the interval ΔE so that the smoothed density Ω is well defined.

(ii) Nevertheless, ΔE is small enough so that it may be regarded as differential within the desired accuracy, i.e., sums can be replaced by integrals.

In the present interpretation, entropy S_m^{Δ} is the logarithm of the number of states compatible with the extensive parameters $(N, E \pm \frac{1}{2}\Delta E, V)$. The canonical partition function Q_c is then obtained as

$$Q_c(N,\beta_r,V) = \sum_E \Delta E\, \Omega(N,E,V) \exp(-\beta_r E) \tag{27}$$

with the same result as (3b) due to (ii).

Another modification of microcanonical entropy is[1]

$$\tilde{S}_m(N,E,V) \equiv \ln\Upsilon(N,E,V) = \ln \int_0^E dE'\, \Omega(N,E',V) \; , \tag{28a}$$

$$\tilde{\alpha} = -\frac{\tilde{\mu}}{\tilde{T}} = \left[\frac{\partial \tilde{S}_m}{\partial N}\right]_{E,V}, \quad \tilde{\beta} = \frac{1}{\tilde{T}} = \left[\frac{\partial \tilde{S}_m}{\partial E}\right]_{N,V}, \tag{28b}$$

$$\tilde{\gamma} = \frac{\tilde{P}}{\tilde{T}} = \left[\frac{\partial \tilde{S}_m}{\partial V}\right]_{N,E}, \quad \tilde{P} = \frac{\tilde{\gamma}}{\tilde{\beta}} = -\left[\frac{\partial E}{\partial V}\right]_{N,\tilde{S}_m} . \tag{28c}$$

For macroscopic systems, $\tilde{s}_m \equiv \tilde{S}_m/N$ converges to $s = S_m/N$, cf. Sec. I. Υ, in the classical approximation also called the phase volume, is dimensionless, but now all states up to energy E are included. This does not reflect the idea of the microcanonical ensemble. On the other hand, $\tilde{S}_m$ and not S_m is adiabatically invariant in the classical case.[1,7,11] Accordingly, $\tilde{P}$ is the *correct mechanical pressure* in isolated classical systems. Additionally, the classical equipartition theorem is fulfilled exactly for $\tilde{T}$, not for T. In the quantum-mechanical case, no analogous statements can be made.[1] Thus, it seems to be preferable to stick to S_m or S_m^{Δ} then. In the classical case, however, the concrete interpretation of pressure favors $\tilde{S}_m$. By the way, the considerations concerning Eq. (24) remain essentially the same when comparing fluctuations of $\tilde{\gamma}$ and $\tilde{P}$ instead of γ and P.

The explicit results for temperature $\tilde{T}$ and pressure $\tilde{P}$ are

$$\tilde{T}=\tilde{\beta}^{-1}=\Upsilon/\Omega,\quad \tilde{P}=\Omega^{-1}\int_0^E dE'(\partial\Omega/\partial V)\ . \tag{29}$$

The new formulas refer to the microcanonical ensemble so far. The extension to other ensembles is simple since the TP fluctuate according to the MP. The probability densities $p_i(N,E,V)$, $i\neq m$, for the MP are the same as in Sec. II. Accordingly, the partition functions Q_i, $i\neq m$, are not changed. They are connected with $\tilde{Q}_m=\Upsilon$ in a similar way as with $Q_m=\Omega$. For instance, integrating by parts yields

$$Q_c=\int_0^\infty dE\,\Omega\exp(-\beta_r E)=\beta_r\int_0^\infty dE\,\Upsilon\exp(-\beta_r E)\ . \tag{30}$$

By means of (29), the resulting $\langle\tilde{T}\rangle_c$ and $\langle\tilde{P}\rangle_c$ are

$$\langle\tilde{\beta}^{-1}\rangle_c=\langle\beta\rangle_c^{-1}=\beta_r^{-1},\ \text{i.e.,}\ \langle\tilde{T}\rangle_c=T_r\ , \tag{31a}$$

$$\langle\tilde{P}\rangle_c=\langle P\beta\rangle_c\beta_r^{-1}=T_r(\partial/\partial V)\ln Q_c\ . \tag{31b}$$

Equation (31a) may be contrasted with (22); as for (31b), cf. Ref. 7. Thus, taking $\langle P\beta\rangle_c=\langle\gamma\rangle_c$ and multiplying by the temperature of the reservoir yields the *true*, i.e., *mechanical pressure* $\langle\tilde{P}\rangle_c$ in the classical case. Starting with $\langle P\rangle_c=\langle\gamma T\rangle_c$, cancellation of errors yields the true pressure if T is thought to be constant T_r in the canonical ensemble. This result will be needed in Sec. VI.

VI. APPLICATION TO COMPUTER EXPERIMENTS

The preceding considerations may answer the question[4–6] "Which formulas for temperature and pressure are the correct ones in computer experiments?" The classical motion of a small number of particles is investigated in computer simulation. Molecular dynamics (MD) usually refers to a restricted microcanonical ensemble (fixed center of mass), Monte Carlo (MC) to the canonical ensemble (only the spatial part being determined explicitly). A detailed discussion of the special features of the MC and MD ensembles is found in Refs. 4–6, but the main aspects of the existing problems can be seen from comparing the classical microcanonical and canonical ensembles.

First we consider three-dimensional systems in the *microcanonical ensemble.* For given N, E, and V, all possible configurations have equal probability.[1] *Configuration* means a specific point in phase space (including momentum). The equipartition theorem yields[1]

$$\tilde{T}N=\tfrac{2}{3}\langle E_{\text{kin}}\rangle_m\ , \tag{32a}$$

$$\tilde{P}V=\tfrac{2}{3}\langle E_{\text{kin}}\rangle_m-\langle W\rangle_m\ . \tag{32b}$$

E_{kin} is the total kinetic energy and W is the virial of a specific configuration,

$$W=\tfrac{1}{3}\sum_{1\le i<j\le N} r_{ij}(\partial\varnothing_{ij}/\partial r_{ij})\ , \tag{33}$$

$\varnothing=\sum\varnothing_{ij}(r_{ij})$ being the pairwise additive potential. Using (32), the fixed $\tilde{T}$ and $\tilde{P}$ can be determined as a microcanonical average (over all configurations) of mechanical quantities. The idea that temperature $\tilde{T}$ fluctuates proportionally to E_{kin} is attractive but incorrect. Analogous arguments hold for pressure $\tilde{P}$. From (32) it follows that

$$\langle\tilde{T}\rangle_i=\tfrac{2}{3}\langle E_{\text{kin}}/N\rangle_i\ , \tag{34a}$$

$$\langle\tilde{P}\rangle_i=\tfrac{2}{3}\langle E_{\text{kin}}/V\rangle_i-\langle W/V\rangle_i \tag{34b}$$

for any ensemble i. Now we compare these results with Refs. 4 and 6. In Ref. 4, the formalism corresponds to Sec. III, the TP are explained as derivatives of the logarithm of the appropriate partition function. For instance, the relation between temperature T (instead of $\tilde{T}$) and kinetic energy is studied for the classical ideal gas. In general, this relation is much more complicated than (34a) and depends on the ensemble and on the interatomic potential. Fluctuations of thermodynamic parameters are not considered in Ref. 4.

In Ref. 6, $M_i^i=\ln Q_i$, Eq. (17), is only accepted for the canonical ensemble. Temperature fluctuations are not considered, only T_r instead of $\langle\tilde{T}\rangle_c$ is used. The true pressure $\langle\tilde{P}\rangle_c$ then results from (31b) or (34b), $i=c$. This justifies the proceeding chosen in Ref. 6. To calculate the pressure in the MD ensemble, using (32b) is called the "common procedure" there. In contrast to our formalism, this is an additional assumption. In any case, pressure $\tilde{P}$ comes out in the MD ensemble and not P as in Ref. 4. Analogously, the small difference in pressure of hard-core systems between MC and MD (Ref. 5) refers to $\tilde{P}$. The statement[4] "small discrepancies in the early hard disk data cannot be due to the difference in ensembles" does not consider this fact. Furthermore, the comparison between Refs. 4 and 6 is difficult since in Ref. 6 T_r and not $\tilde{T}$ is also used in the *appropriate* MD ensemble: In both references, $E_{MD}=\langle E\rangle_c$, the number of particles and volume are also the same for an appropriate comparison. The total energy being the same, differences in $\langle E_{\text{kin}}\rangle$ and $\langle W\rangle$ occur, hence the *ensemble corrections*[6] for these quantities and thus the pressure. Incidentally, further possibilities to calculate $\tilde{P}$ in MD simulations are discussed in Refs. 13 and 14.

In another paper, temperature fluctuations during a MC experiment are really taken into account.[15] If the system is not too small, fluctuations of pressure and potential energy are small and thus essentially linear functions of temperature fluctuation. In fact, subaveraged values of pressure and potential energy turned out to be connected by a linear relation for the model liquid considered. The superimposed statistical scatter comes from the fact that potential energy and virial of a single configuration are well defined, but not the pressure. Using (34) in the form

$$\tilde{P}_{\text{single}}=(NT_r-W_{\text{single}})/V \tag{35}$$

yields an *unbiased estimate* of $\tilde{P}$ based on a single configuration, but *not the pressure of this configuration itself.* Accordingly, apparent "pressure fluctuations" in computer experiments have to be distinguished from proper fluctuations, Secs. IV and V.

In this paper, thermodynamic parameters and their fluctuations have been studied. For instance, T and $\tilde{T}$ are possible extensions of temperature to finite systems. Interpreting pressure mechanically and not only thermodynamically is the key deciding which of the formalisms considered has to be preferred.

ACKNOWLEDGMENTS

The author is grateful to Professor P. Weinzierl for continuous interest in this work. Financial support has been given by the Austrian Science Research Council (Fonds zur Förderung der wissenschaftlichen Forschung) Grant No. P4710.

---

[1] A. Münster, *Statistical Thermodynamics* (Springer, Berlin, 1969), Vol. 1, Chaps. 1—3.

[2] L. D. Landau and E. M. Lifshitz, *Statistical Physics* (Pergamon, New York, 1969), Chap. 12.

[3] T. L. Hill, *Statistical Thermodynamics* (Addison-Wesley, Reading, Mass., 1960), p. 33.

[4] F. Lado, J. Chem. Phys. **75**, 5461 (1981).

[5] J. J. Erpenbeck and W. W. Wood, in *Statistical Mechanics,* edited by B. J. Berne (Plenum, New York, 1977), Part B, Chap. 1.

[6] D. D. Wallace and G. K. Straub, Phys. Rev. A **27**, 2201 (1983).

[7] J. E. Kilpatrick, in *Physical Chemistry,* edited by H. Eyring (Academic, New York, 1967), Vol. 2, Chap. 1.

[8] T. L. Hill, *Thermodynamics of Small Systems* (Benjamin, New York, 1963), Vol. 1, p. 19.

[9] E. T. Jaynes, Phys. Rev. **106**, 620 (1957).

[10] R. A. Sack, Mol. Phys. **2**, 8 (1959).

[11] J. Stephenson, Physica **117A**, 593 (1983).

[12] R. Kubo, *Statistical Mechanics* (North-Holland, Amsterdam, 1971), Chap. 1.

[13] A. Klemm, Z. Naturforsch. **33A**, 778 (1978).

[14] D. H. Tsai, J. Chem. Phys. **70**, 1375 (1979).

[15] N. Quirke and G. Jacucci, Mol. Phys. **45**, 823 (1982).