On the relationship between principal fluctuations and stability coefficients in multicomponent systems

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There is a univocal correspondence between each of the $(n+2)!$ stability coefficients of an n-component system and mean squared fluctuations of Gibbs-space variables (entropy, volume, molecule number) in which the subsystem under study is defined through a single extensive Gibbs-space variable (principal fluctuations). The relationship between principal fluctuations and stability coefficients [Eq. (53)] is derived in this paper starting from the usual expressions involving explicit calculation of the inverse of an $(n+1)\times(n+1)$ matrix. A general equation between higher order energy variations in fluctuating subsystems [Eq. (22)] is also derived. The relationship between principal fluctuations and stability coefficients yields, as particular cases, expressions which had been used previously for the limiting case of single-component systems, or extended to solutions through heuristic arguments.

INTRODUCTION: THERMODYNAMICS OF FLUCTUATIONS

In axiomatic thermodynamics, the equilibrium state attained by a closed macroscopic system, in the absence of external force fields or inertial forces, is fully characterized by two nonconjugate properties and the masses of the different components initially in the system. (This refers to a set of postulates[4] among which we do not include a probabilistic interpretation for entropy. In Callen's approach,[9] expressions for Gibbs-space variable fluctuations follow from an additional postulate; we emphasize, rather, the relationship between subsystem definition and stability coefficients.) Specification of two conjugate properties (temperature and entropy, pressure and volume, chemical potential and mole number) can lead to ambiguities: the state of a unit mass of a substance exhibiting density maxima is not uniquely specified by its pressure and volume in the region where density maxima occur; no ambiguity exists, however, if a nonconjugate pair, such as temperature and volume, is selected.

In this paper, we will consider nonreacting, single phase, multicomponent systems, with no internal barriers to the transfer of mass or energy, or to the attainment of mechanical equilibrium. At equilibrium, all intensive properties are uniform throughout such a system.

This introductory section includes the use of a new relationship: Eq. (22); the thermodynamics of fluctuations is discussed here at some length so as to make the overall treatment consistent, and, as far as possible, self-contained.

The equilibrium states of a unit mass of an n-component system can be represented as an $(n+2)$-dimensional hypersurface $(u, s, v, y_1,...,y_{n-1})$, where y_i is a mole fraction, and lower case denotes the specific value of an extensive property (e.g., volume per molecule). If we consider, for pictorial simplicity, a single component system, we can visualize the energy–entropy projection of a constant volume intersection of the three-dimensional (u, s, v) surface. This is shown schematically in Fig. 1. Point a represents an equilibrium state: its entropy (energy) is therefore a maximum (minimum) with respect to possible variations at constant mass, volume, and energy (entropy).

For nonreacting, single phase, multicomponent systems, a nonequilibrium state corresponds to a nonuniformity in some intensive property of the system. Because we want to study the problem thermodynamically, we restrict our attention to situations where local equilibrium can be assumed: properties change over length scales which are large compared with the molecules' mean free path. We can then divide the system under study into various subsystems, each of which can be described thermodynamically.[1] We represent nonequilibrium states[2] by weighing the properties of each subsystem by the corresponding mass fractions (i.e., mass of subsystem/total mass). Points representing the various subsystems at equilibrium, therefore, lie on the surface corresponding to the equilibrium states of the given system; their mass fraction-weighted center of mass lies outside the surface, since it corresponds to a nonequilibrium state. If we imagine, e.g., a density nonuniformity within a system of given total energy and volume, we obtain a point such as b.

Thermodynamically, then, we study fluctuations by analyzing the energetics of a change such as ab. A system initially in a nonequilibrium "state" such as b will spontaneously and irreversibly relax to state a, if isolated. In the limiting case of a reversible and adiabatic relaxation, the sys-

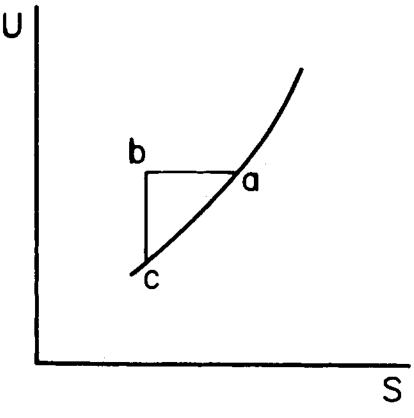

FIG. 1. Schematic U–S projection showing isochore (line ac), equilibrium states (a,c), reversible (b⟶c) and irreversible (b⟶a) adiabatic relaxation processes.

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tem's entropy is unaltered, and $U_b - U_c$ is the maximum work that can be obtained from this reversible relaxation to a (different) equilibrium state (c). At constant total volume and mass we can write, for small deviations from equilibrium,

$$\frac{U_b - U_c}{S_a - S_b} \approx \left(\frac{\partial U}{\partial S}\right)_{V,N} = T_0, \tag{1}$$

where T_0 is the equilibrium temperature of the system and N, the number of molecules. Equation (1)[1] is central to the developments that follow, and relates the entropy change associated with a given fluctuation to the maximum work obtainable from the corresponding relaxation.

The system under study (Σ) can always be imagined as being composed of a subsystem (σ) which, because of fluctuations, is not in equilibrium with the rest of the system (Ω). It is always possible to imagine Ω such that $\Omega \gg \sigma$, although we require that σ be macroscopic.

If we interpret the second law as a nonstatistical postulate, a macroscopic fluctuation is impossible. We then "construct" the nonequilibrium state (b) from a small but macroscopic system (σ) which is brought into contact with a much larger system (Ω) with different intensive properties (a). If we impose the isolation constraint, relaxation will occur upon elimination of the barriers separating σ and Ω (i.e., membranes, rigid walls, etc.) in such a way that, as the ratio Ω/σ becomes larger, the changes in Ω become smaller. We will quantify the energetics of this effect later [i.e., Eq. (22)].

Consider a reversible, isentropic process such as $c \to b$, in a single-phase, multicomponent system. We are interested in calculating $\Delta U^{\Sigma} = U_b - U_c$. Because the process is reversible and isentropic, we can write

$$\Delta U^{\Sigma} = U_b - U_c = -\delta W \tag{2}$$

or, as we said before, ΔU represents the minimum work required in order to bring about the change $c \to b$ (or the maximum work that can be obtained from the relaxation $b \to c$). The energy change can be written as

$$\Delta U = \delta U + \frac{1}{2!}\delta^2 U + \cdots. \tag{3}$$

The linear term vanishes identically because c is an equilibrium state. Third and higher order terms are negligible away from limits of stability, therefore,

$$\Delta U^{\Sigma} = \tfrac{1}{2}\delta^2 U^{\Sigma} = \tfrac{1}{2}(\delta^2 U^{\sigma} + \delta^2 U^{\Omega}). \tag{4}$$

A relationship between $\delta^2 U^{\sigma}$ and $\delta^2 U^{\Omega}$ will now be derived. In general, we can write (with λ denoting σ or Ω, and using Einstein notation)

$$\delta^2 U^{\lambda} = U^{\lambda}_{ij}\, \delta X^{\lambda}_i \delta X^{\lambda}_j \quad (i = 1,\ldots,n+2), \tag{5}$$

$$U^{\lambda} = U^{\lambda}(X^{\lambda}_1, X^{\lambda}_2,\ldots, X^{\lambda}_{n+2}) = U^{\lambda}(S^{\lambda}, V^{\lambda}, N^{\lambda}_1,\ldots, N^{\lambda}_n), \tag{6}$$

where

$$U^{\lambda}_{ij} = \frac{\partial^2 U^{\lambda}}{\partial X^{\lambda}_i \partial X^{\lambda}_j}. \tag{7}$$

We introduce the notation

$$\xi_i = \left(\frac{\partial U}{\partial X_i}\right)_{X[i]}, \tag{8}$$

where $X[i]$ denotes all X's constant except for X_i. To illustrate Eq. (8), we write, e.g.,

$$X_1 = S \Rightarrow \xi_1 = T, \tag{9}$$

$$X_2 = V \Rightarrow \xi_2 = -P, \tag{10}$$

$$X_{j+2} = N_j \Rightarrow \xi_{j+2} = \mu_j \quad (j = 1,\ldots,n). \tag{11}$$

With the above notation, we consider the quantity

$$N^{\Omega}\frac{\partial}{\partial X^{\Omega}_j}\left[\left(\frac{\partial U^{\Omega}}{\partial X^{\Omega}_i}\right)_{X[i]}\right]_{X[j]} = N^{\Omega} U^{\Omega}_{ij} = N^{\Omega}\left(\frac{\partial \xi^{\Omega}_i}{\partial X^{\Omega}_j}\right)_{X[j]}, \tag{12}$$

where N^{Ω} is the total number of molecules in Ω. X^{Ω}_j can represent S^{Ω}, V^{Ω}, or N^{Ω}_j $(j = 1,\ldots,n)$. If $X_j \neq N_j$,

$$N^{\Omega}\left(\frac{\partial \xi^{\Omega}_i}{\partial X^{\Omega}_j}\right)_{X[j]} = \frac{N^{\Omega}}{N^{\Omega}}\left(\frac{\partial \xi^{\Omega}_i}{\partial x^{\Omega}_j}\right)_{N^{\Omega}, X[j]}, \tag{13}$$

where

$$x_j \equiv X_j/N, \tag{14}$$

i.e., an intensive property. If $X_j \neq N_j$, then, the left-hand side of Eq. (13) is equal to an intensive property. Because we are expanding about an equilibrium state (c), all intensive properties are identical in σ and Ω at c. We now consider the case $X_j = N_j$, and write the generic mole fraction,

$$y^{\lambda}_j = \frac{N^{\lambda}_j}{N^{\lambda}}, \tag{15}$$

$$\left(\frac{\partial y^{\lambda}_j}{\partial N^{\lambda}_j}\right)_{N[j]} = \frac{(1 - y^{\lambda}_j)}{N^{\lambda}}, \tag{16}$$

therefore,

$$N^{\Omega}\left(\frac{\partial \xi^{\Omega}_i}{\partial X^{\Omega}_j}\right)_{X[j]} = N^{\Omega}\left(\frac{\partial \xi^{\Omega}_i}{\partial N^{\Omega}_j}\right)_{S^{\Omega}, V^{\Omega}, N^{\Omega}[j]}$$

$$= (1 - y^{\Omega}_j)\left(\frac{\partial \xi^{\Omega}_i}{\partial y^{\Omega}_j}\right)_{S^{\Omega}, V^{\Omega}, N^{\Omega}[j]} \tag{17}$$

which is also an intensive property. Therefore, it is always true that

$$N^{\Omega} U^{\Omega}_{ij} = N^{\sigma} U^{\sigma}_{ij}. \tag{18}$$

The $c \to b$ process takes place at constant total mass, entropy, and volume, therefore, we can write, for nonreacting systems,

$$\delta X^{\sigma}_i \delta X^{\sigma}_j = \delta X^{\Omega}_i \delta X^{\Omega}_j \tag{19}$$

so that, finally

$$\delta^2 U^{\Sigma} = \delta^2 U^{\sigma} + \delta^2 U^{\Omega} = U^{\sigma}_{ij}\delta X^{\sigma}_i \delta X^{\sigma}_j + U^{\Omega}_{ij}\delta X^{\Omega}_i \delta X^{\Omega}_j$$

$$= \delta X^{\sigma}_i \delta X^{\sigma}_j\left(U^{\sigma}_{ij} + \frac{N^{\sigma}}{N^{\Omega}} U^{\sigma}_{ij}\right) = \left(1 + \frac{N^{\sigma}}{N^{\Omega}}\right)\delta^2 U^{\sigma}, \tag{20}$$

or, in other words,

$$N^{\sigma}\delta^2 U^{\sigma} = N^{\Omega}\delta^2 U^{\Omega}. \tag{21}$$

Equation (21) is a particular case of the general relationship

$$(N^{\sigma})^{m-1}\delta^m U^{\sigma} = (-1)^m (N^{\Omega})^{m-1}\delta^m U^{\Omega}, \tag{22}$$

where m is any arbitrary integer; Eq. (22) is derived in Appendix A.

The minimum work required in order to bring about a nonequlibrium state isentropically, starting from equilibrium, is then a second order quantity (and therefore the same is true for the maximum work that can be obtained from a relaxation when the latter is constrained to be reversible).

We now return to Eq. (1) which, in the light of the previous developments, can now be written

$$T_0(S_a - S_b) = U_b - U_c = \tfrac{1}{2}(1 + N^\sigma/N^\Omega)\delta^2 U^\sigma, \tag{23}$$

where T_0 characterizes Ω, which acts like a reservoir in the limit $N^\Omega \gg N^\sigma$ for which T_0 is unchanged. The fluctuation $a \rightarrow b$ has an associated probability of occurence[3]

$$p \sim \exp[(S_b - S_a)/k], \tag{24}$$

therefore,

$$p \sim \exp\left[-\frac{\beta}{2}\left(1 + \frac{N^\sigma}{N^\Omega}\right)\delta^2 U^\sigma\right], \tag{25}$$

$$\beta \equiv \frac{1}{kT_0}.$$

The factor $(1 + N^\sigma/N^\Omega)$ becomes unity in the limit we are considering ($N^\sigma \ll N^\Omega$, for which β becomes a parameter characteristic of the reservoir); it will therefore not be included in what follows. In addition, we note that its presence would merely give rise to the following positive multiplicative constants, all of which approach unity in the above mentioned limit: $(1 + N^\sigma/N^\Omega)^{(n+1)/2}$ [the right-hand side of Eq. (28)], and $(1 + N^\sigma/N^\Omega)^{-1}$ [the right-hand side of Eqs. (29)–(31)] (see below). We therefore write, for $\sigma \ll \Omega$,

$$p \sim \exp\left(-\frac{\beta\delta^2 U^\sigma}{2}\right). \tag{26}$$

This is the fundamental equation of fluctuation theory.[1]

The mathematical conditions under which the quadratic form $\delta^2 U$ loses its positive–definite character are the criteria of stability (or stability coefficients). In fluctuation theory, on the other hand, we are interested in determining the average magnitude of fluctuations of thermodynamic quantities about their equilibrium values. The connection between the two approaches lies in the general relationship between fluctuations of Gibbs-space variables (S, V, N_i) and stability coefficients. We will derive this relationship below, for an arbitrary n-component mixture.

If we are to study fluctuations occuring in σ, we must first define σ. In the present context, this means that some arbitrary extensive property is fixed, and we study fluctuations in thermodynamic properties occurring within this arbitrarily defined system. For example, σ can be an arbitrarily defined region in space, or a system containing a given number of molecules. Other definitions are obviously possible, and will be discussed below (see the Operational Definitions section). What is important here is that, in defining σ, we are fixing the value of one of the $n + 2$ Gibbs-space variables. Therefore, U^σ is now effectively a function of $n + 1$ variables, since one of them is not allowed to vary and all partial derivatives are at constant X_{n+2}. It is clearly meaningless to speak about fluctuations within an undefined system.

We have used classical (axiomatic) thermodynamics as far as possible [i.e., up to Eq. (24)]. The position of fluctuation theory vis-a-vis statistical mechanics and axiomatic thermodynamics deserves further attention. Fluctuations can, of course, be studied from a purely statistical perspective. On the other hand, although thermodynamics provides a useful theoretical framework, there are two important qualifications that must be taken into consideration. In the first place, the probabilistic interpretation of entropy [from which Eq. (24) results] is extraneous to axiomatic thermodynamics. In the second place, we are restricting our analysis to small fluctuations: this requires that we consider cases where $\Delta S/S$ is small. In axiomatic thermodynamics, however, the denominator (S) is completely arbitrary, and only the numerator is determined for a process such as $a \rightarrow b$. The concept of a small fluctuation, therefore, is undefined in axiomatic thermodynamics.

Superscript σ can be dropped from Eq. (26): the choice of σ is obviously arbitrary. For macroscopic systems, furthermore, the equilibrium state is overwhelmingly probable: this implies a sharply peaked fluctuation distribution function; because of this, we can write, with vanishing error in the thermodynamic limit

$$1 = A\int_{-\infty}^{\infty}\ldots\int_{-\infty}^{\infty}\exp\left[-\frac{1}{2kT_0}U_{ij}\delta X_i\delta X_j\right] \times d(\delta X_1)\ldots d(\delta X_{n+1}), \tag{27}$$

where A is a normalization constant, and X_{n+2} does not vary. Equation (27) signifies that fluctuations are distributed according to a multivariate Gaussian. From this we can at once write the following relations, which we give without proof (see, for example, Ref. 1):

$$A = (\beta/2\pi)^{(n+1)/2} D^{1/2}, \tag{28}$$

$$\langle\delta\xi_i\delta\xi_j\rangle = kT_0 \mathrm{D}_{ij}, \tag{29}$$

$$\langle\delta\xi_i\partial X_j\rangle = kT_0\delta_{ij}, \tag{30}$$

$$\langle\delta X_i\delta X_j\rangle = kT_0\mathrm{D}_{ij}^{-1}, \tag{31}$$

where ξ_i has already been defined, δ_{ij} is Kronecker's delta, and D, D_{ij}, and D_{ij}^{-1} denote, respectively, the determinant, (ij)th element, and (i,j)th element of the inverse of the matrix

$$\mathrm{D} = \begin{bmatrix} U_{11} & U_{12}\cdots & U_{1,n+1} \\ U_{21} & U_{22}\cdots & U_{2,n+1} \\ \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot \\ U_{n+1,1} & U_{n+1,2}\cdots & U_{n+1,n+1} \end{bmatrix} = \frac{\partial(\xi_1,\ldots,\xi_{n+1})}{\partial(X_1,\ldots,X_{n+1})}, \tag{32}$$

where all partial derivatives are at constant X_{n+2}. We define $\langle\delta X_i^2\rangle$ as a principal fluctuation, that is to say, a mean squared fluctuation of a Gibbs-space variable within a subsystem whose extent is defined by one and only one variable (X_{n+2}).

We note that the X_i's can only be Gibbs-space variables, since these constitute the only nonconjugate set of extensive properties in terms of which U is uniquely defined, and the fact that the X_i's are extensive has been used in Eq. (19). The ordering of the X_i's, on the other hand, is obviously arbitrary.

PRINCIPAL FLUCTUATIONS AND STABILITY

Before proceeding with the discussion of the general relationship between principal fluctuations and stability coefficients, we recall that, for an n-component mixture, the second order partial derivative

$$\phi^{(n)}_{n+1,n+1} \equiv \left(\frac{\partial \xi_{n+1}}{\partial X_{n+1}}\right)_{\xi_1 \to \xi_n, X_{n+2}} = \left(\frac{\partial^2 \phi^{(n)}}{\partial X^2_{n+1}}\right)_{\xi_1 \to \xi_n, X_{n+2}}, \tag{33}$$

where

$$\phi^{(n)} \equiv \phi^{(n)}(\xi_1, \xi_2, \ldots, \xi_n, X_{n+1}, X_{n+2}) = \phi^{(0)} - \sum_{i=1}^{n} \xi_i X_i \tag{34}$$

and

$$\phi^{(0)} = U(X_1, \ldots, X_{n+2}) = U(S, V, N_1, \ldots, N_n) \tag{35}$$

is called a stability coefficient, and is of central importance in the theory of thermodynamic stability. In the above equations, $\phi^{(n)}$ is the nth Legendre transform of the fundamental equation in its energy representation, or, more appropriately, the nth Legendre transform of the system's energy.

Stability coefficients are positive for stable or metastable states, and vanish identically at the limit of stability. Because $(n+2)$ variables can be ordered arbitrarily, there are $(n+2)!$ equivalent stability coefficients which vanish simultaneously at the limit of stability. As an example, the six criteria for a pure substance are

$$\left(\frac{\partial P}{\partial V}\right)_{T,N} < 0, \tag{36}$$

$$\left(\frac{\partial \mu}{\partial N}\right)_{T,V} > 0, \tag{37}$$

$$\left(\frac{\partial T}{\partial S}\right)_{P,N} > 0, \tag{38}$$

$$\left(\frac{\partial \mu}{\partial N}\right)_{P,S} > 0, \tag{39}$$

$$\left(\frac{\partial T}{\partial S}\right)_{\mu,V} > 0, \tag{40}$$

$$\left(\frac{\partial P}{\partial V}\right)_{\mu,S} < 0. \tag{41}$$

In this paper we do not derive the theory that leads to Eqs. (36)–(41); a thorough discussion can be found elsewhere.[4] We emphasize that although each stability coefficient is expressed in terms of different thermodynamic variables, they all vanish simultaneously along the limit of stability locus (i.e., the spinodal curve); in this sense, stability coefficients merely express the same fact in terms of different variables: this will be shown to be rigorously true when we discuss the connection between principal fluctuations and stability coefficients.

We will now derive the following relationship between principal fluctuations and stability coefficients in an n-component mixture:

$$\langle(\delta X_{n+1})^2\rangle_{X_{n+2}} = \frac{kT_0}{(\partial \xi_{n+1}/\partial X_{n+1})_{\xi_1 \to \xi_n, X_{n+2}}}. \tag{42}$$

In Eq. (42), subscript X_{n+2} on the left-hand side denotes the particular extensive variable whose constancy defines σ. Although Eq. (42) will be derived mathematically, and is therefore of general validity, some choices of X_{n+2} give rise to operational definitions of principal fluctuations that have an immediate physical interpretation, whereas other choices define principal fluctuations that can be calculated but not directly measured. We will discuss this below (see the Operational Definitions section).

To show the general relationship between mean squared principal fluctuations and stability coefficients, we first write the general stability coefficient as a ratio of Jacobians,

$$\phi^{(n)}_{n+1,n+1} = \left(\frac{\partial \xi_{n+1}}{\partial X_{n+1}}\right)_{\xi_1 \to \xi_n, X_{n+2}} = \frac{\partial(\xi_1, \ldots, \xi_{n+1})/\partial(X_1, \ldots, X_{n+1})}{\partial(\xi_1, \ldots, \xi_n)/\partial(X_1, \ldots, X_n)}. \tag{43}$$

Equation (43) can be derived via a diagonalization procedure[5] based on successive applications of chain rule

$$\frac{\partial(\xi_1, \ldots, \xi_n)}{\partial(X_1, \ldots, X_n)} = \frac{\partial(\xi_1, \ldots, \xi_n)}{\partial(\xi_1, \ldots, \xi_{n-1}, X_n)} \cdot \frac{\partial(\xi_1, \ldots, \xi_{n-1}, X_n)}{\partial(X_1, \ldots, X_n)}. \tag{44}$$

Equation (44) can be rewritten as follows:

$$\begin{vmatrix} 1 & 0 \ldots\ldots\ldots\ldots 0 & 0 \\ 0 & 1 \ldots\ldots\ldots\ldots 0 & 0 \\ \cdot & \cdot \qquad\qquad\qquad \cdot & \cdot \\ \cdot & \cdot \qquad\qquad\qquad \cdot & \cdot \\ \cdot & \cdot \qquad\qquad\qquad \cdot & \cdot \\ \cdot & \cdot \qquad\qquad\qquad \cdot & \cdot \\ 0 & 0 \ldots\ldots\ldots\ldots 1 & 0 \\ \left(\frac{\partial \xi_n}{\partial \xi_1}\right)_{\xi_2, \ldots, \xi_{n-1}, X_n, \ldots, X_{n+2}} & \ldots\ldots\ldots\ldots\ldots & \left(\frac{\partial \xi_n}{\partial X_N}\right)_{\xi_1, \ldots, \xi_{n-1}, X_{n+1}, X_{n+2}} \end{vmatrix}$$

$$\times \frac{\partial(\xi_1, \ldots, \xi_{n-1}, X_n)}{\partial(X_1, \ldots, X_n)} = \left(\frac{\partial \xi_n}{\partial X_n}\right)_{\xi_1, \ldots, \xi_{n-1}, X_{n+1}, X_{n+2}} \cdot \frac{\partial(\xi_1, \ldots, \xi_{n-1}, X_n)}{\partial(X_1, \ldots, X_n)}, \tag{45}$$

where constancy of X_{n+1} and X_{n+2} in the partial derivatives follows from the fact that $\phi^{(0)}$ is a function of $(n+2)$ variables although not all of them are free to vary (see above). The numerator and denominator of Eq. (43) can therefore be expressed as

$$\frac{\partial(\xi_1,\ldots,\xi_{n+1})/\partial(X_1,\ldots,X_{n+1})}{\partial(\xi_1,\ldots,\xi_n)/\partial(X_1,\ldots,X_n)} = \frac{(\partial\xi_{n+1}/\partial X_{n+1})_{\xi_1,\ldots,\xi_n,X_{n+2}}\,(\partial\xi_n/\partial X_n)_{\xi_1,\ldots,\xi_{n-1},X_{n+1},X_{n+2}}\cdots(\partial\xi_1/\partial X_1)_{X_2,\ldots,X_{n+2}}}{(\partial\xi_n/\partial X_n)_{\xi_1,\ldots,\xi_{n-1},X_{n+1},X_{n+2}}\cdots(\partial\xi_1/\partial X_1)_{X_2,\ldots,X_{n+2}}} = (\partial\xi_{n+1}/\partial X_{n+1})_{\xi_1,\ldots,\xi_n,X_{n+2}}\,. \tag{46}$$

This completes the first part of our proof. We will now show the relationship between mean squared fluctuations of Gibbs-space variables $(S, V, N_i,\ldots,N_l)$ and stability coefficients. To this end, we write Eq. (31) for the case $i = j$,

$$\langle(\delta X_j)^2\rangle_{X_{n+2}} = kT_0\mathrm{D}_{jj}^{-1} \tag{47}$$

or explicitly,

$$\langle(\delta X_j)^2\rangle = kT_0\frac{\begin{vmatrix} U_{11}\cdots & U_{1,j-1} & U_{1,j+1}\cdots & U_{1,n+1}\\ \vdots & \vdots & \vdots & \vdots\\ U_{j-1,1}\cdots & U_{j-1,j-1} & U_{j-1,j+1}\cdots & U_{j-1,n+1}\\ U_{j+1,1}\cdots & U_{j+1,j-1} & U_{j+1,j+1} & U_{j+1,n+1}\\ \vdots & \vdots & \vdots & \vdots\\ U_{n+1,1}\cdots & U_{n+1,j-1} & U_{n+1,j+1}\cdots & U_{n+1,n+1}\end{vmatrix}}{\begin{vmatrix} U_{11} & U_{12}\cdots\cdots & U_{1,n+1}\\ U_{21} & U_{22}\cdots\cdots & U_{2,n+1}\\ \vdots & \vdots & \vdots\\ U_{n+1,1} & U_{n+1,2}\cdots\cdots & U_{n+1,n+1}\end{vmatrix}}\,. \tag{48}$$

We will now prove that the ratio of determinants in Eq. (48) is the reciprocal of the corresponding quantity in Eq. (43). We first reorder the $(n+1)$ variables, and establish the following correspondence between the ordering indices:

Old	1	2	...	$j-1$	$j+1$	...	$n+1$	j	$n+2$
Reordered	1	2		$j-1$	j		n	$n+1$	$n+2$

which simply defines an index relabeling operator. We denote this operator by g, and write, formally,

$$i(\text{old}) \xrightarrow{g} k\,(\text{new}). \tag{49}$$

It is easy to see that, when acted upon by g, the numerator of Eq. (48) becomes

$$\begin{vmatrix} U_{11}\cdots & U_{1,j-1} & U_{1,j+1}\cdots & U_{1,n+1}\\ \vdots & \vdots & \vdots & \vdots\\ U_{j-1,1}\cdots & U_{j-1,j-1} & U_{j-1,j+1}\cdots & U_{j-1,n+1}\\ U_{j+1,1}\cdots & U_{j+1,j-1} & U_{j+1,j+1}\cdots & U_{j+1,n+1}\\ \vdots & \vdots & \vdots & \vdots\\ U_{n+1,1}\cdots & U_{n+1,j-1} & U_{n+1,j+1}\cdots & U_{n+1,n+1}\end{vmatrix} \xrightarrow{g} \begin{vmatrix} U_{11}\cdots & U_{1,j-1} & U_{1,j}\cdots & U_{1,n}\\ \vdots & \vdots & \vdots & \vdots\\ U_{j-1,1}\cdots & U_{j-1,j-1} & U_{j-1,j}\cdots & U_{j-1,n}\\ U_{j,1}\cdots & U_{j,j-1} & U_{j,j}\cdots & U_{j,n}\\ \vdots & \vdots & \vdots & \vdots\\ U_{n,1}\cdots & U_{n,j-1} & U_{n,j}\cdots & U_{nn}\end{vmatrix}, \tag{50}$$

which we recognize as the denominator of Eq. (43). The denominator in Eq. (48), on the other hand, is transformed by g as follows:

$$\begin{vmatrix} U_{11} & U_{12}\cdots & U_{1n} & U_{1,n+1}\\ U_{21} & U_{22}\cdots & U_{2n} & U_{2,n+1}\\ \vdots & \vdots & \vdots & \vdots\\ U_{n1} & U_{n2}\cdots & U_{nn} & U_{n,n+1}\\ U_{n+1,1} & U_{n+1,2}\cdots & U_{n+1,n} & U_{n+1,n+1}\end{vmatrix} \xrightarrow{g} \begin{vmatrix} U_{11}\cdots & U_{1,j-1} & U_{1,n+1} & U_{1,j}\cdots & U_{1,n}\\ U_{21}\cdots & U_{2,j-1} & U_{2,n+1} & U_{2,j}\cdots & U_{2,n}\\ \vdots & \vdots & \vdots & \vdots & \vdots\\ U_{j-1,1}\cdots & U_{j-1,j-1} & U_{j-1,n+1} & U_{j-1,j}\ldots & U_{j-1,n}\\ U_{n+1,1}\cdots & U_{n+1,j-1} & U_{n+1,n+1} & U_{n+1,j}\cdots & U_{n+1,n}\\ U_{j,1}\cdots & U_{j,j-1} & U_{j,n+1} & U_{j,j}\cdots & U_{j,n}\\ \vdots & \vdots & \vdots & \vdots & \vdots\\ U_{n1}\cdots & U_{n,j-1} & U_{n,n+1} & U_{nj}\cdots & U_{n,n}\end{vmatrix}\,. \tag{51}$$

We emphasize the fact that, in Eqs. (50) and (51), the left-hand sides refer to second order partial derivatives with respect to variables labeled according to the "old" convention, whereas the right-hand sides contain exactly the same derivatives, but the variables have now been relabeled according to the "reordered" convention.

The reordered determinant [the right-hand side of Eq. (51)] is identical to the numerator of Eq. (43). This can be seen by noting that its jth column (with elements $U_{i,n+1}$) can be moved to the last position, and becomes the $(n+1)$th column, through $(n-j+1)$ successive column interchanges, each of which merely changes the determinant's sign. Similarly, the jth row of this partially transformed determinant (with elements $U_{n+1,i}$) can be moved to the last position, and become the $(n+1)$th row, through $(n-j+1)$ successive row interchanges, each of which merely changes the determinant's sign, so that, after $(n-j+1)$ column and $(n-j+1)$ row interchanges we have finally,

$$\begin{vmatrix} U_{11}\cdots & U_{1,j-1} & U_{1,n+1} & U_{1,j}\cdots & U_{1,n} \\ U_{21}\cdots & U_{2,j-1} & U_{2,n+1} & U_{2,j}\cdots & U_{2,n} \\ \vdots & \vdots & \vdots & \vdots & \vdots \\ U_{j-1,1}\cdots & U_{j-1,j-1} & U_{j-1,n+1} & U_{j-1,j}\cdots & U_{j-1,n} \\ U_{n+1,1}\cdots & U_{n+1,j-1} & U_{n+1,n+1} & U_{n+1,j}\cdots & U_{n+1,n} \\ U_{j,1}\cdots & U_{j,j-1} & U_{j,n+1} & U_{j,j}\cdots & U_{j,n} \\ \vdots & \vdots & \vdots & \vdots & \vdots \\ U_{n1}\cdots & U_{n,j-1} & U_{n,n+1} & U_{n,j}\cdots & U_{n,n} \end{vmatrix} = \begin{vmatrix} U_{11}\cdots & U_{1,j-1} & U_{1,j}\cdots & U_{1,n} & U_{1,n+1} \\ U_{21}\cdots & U_{2,j-1} & U_{2,j}\cdots & U_{2,n} & U_{2,n+1} \\ \vdots & \vdots & \vdots & \vdots & \vdots \\ U_{j-1,1}\cdots & U_{j-1,j-1} & U_{j-1,j}\cdots & U_{j-1,n} & U_{j-1,n+1} \\ U_{j,1}\cdots & U_{j,j-1} & U_{j,j}\cdots & U_{j,n} & U_{j,n+1} \\ \vdots & \vdots & \vdots & \vdots & \vdots \\ U_{n,1}\cdots & U_{n,j-1} & U_{n,j}\cdots & U_{n,n} & U_{n,n+1} \\ U_{n+1,1}\cdots & U_{n+1,j-1} & U_{n+1,j}\cdots & U_{n+1,n} & U_{n+1,n+1} \end{vmatrix} \tag{52}$$

which completes the proof. Both determinants in Eq. (52) now refer to variables labeled according to the reordered convention. The relation we have just proved can therefore be written, in its most general form, as

$$\langle(\delta X_{n+1})^2\rangle_{X_{n+2}} = kT_0\left[\left(\frac{\partial \xi_{n+1}}{\partial X_{n+1}}\right)_{\xi_1\to\xi_n, X_{n+2}}\right]^{-1}, \tag{53}$$

where the same ordering convention now applies to the left- and right-hand sides.

Through Eq. (53), then, we can calculate fluctuations of entropy, volume, and molecule numbers in multicomponent systems, corresponding to situations where the subsystem under study is defined by its entropy, volume, or molecule number of a specific component. For any mixture there is a one-to-one correspondence between these fluctuations and stability coefficients. Equation (53) allows the calculation of Gibbs-space variable fluctuations without inverting a matrix [Eq. (31)] and thus reduces the number of partial derivatives to be computed from $(n+1)(n+2)/2$ to one.

At limits of stability, principal fluctuations diverge, and stability coefficients vanish, but the quantitative accuracy of Eq. (53) breaks down, since the situation for which it was derived (small fluctuations) no longer applies.

The denominator of Eq. (53) is obviously a second order partial derivative of a potential function with arguments $\xi_1\to\xi_n, X_{n+1}, X_{n+2}$, with respect to X_{n+1}. We can regard this as an appropriate free energy, in which case we recover, among the many particular cases, the form of the expression used by Tolman,[6] who extended Einstein's work on critical opalescence[7] to concentration fluctuations in solutions. Tolman argued that, in this case, the fluctuating subsystem should be represented by a grand canonical ensemble, thus imposing (and not deriving) the T, V, $\mu_{[i]}$ constraints *a priori*: his result is Eq. (63), a particular case of Eq. (53), which provides a rigorous definition of the appropriate "free energy" in all cases, and shows explicitly the correspondence between principal fluctuations and stability coefficients.

A constraint that gives rise to fluctuations with an obvious physical interpretation is $X_{n+2} = V$. In this case, we study fluctuations occurring within a fixed region in space. As an example, for a ternary mixture, we write

$$\langle \delta S^2\rangle_V = \frac{kT_0}{(\partial T/\partial S)_{\mu_1,\mu_2,\mu_3,V}}, \tag{54}$$

$$\langle(\delta N_1)^2\rangle_V = \frac{kT_0}{(\partial\mu_1/\partial N_1)_{T,\mu_2,\mu_3,V}} \tag{55}$$

with analogous expressions for N_2 and N_3. To obtain expressions for principal fluctuations, therefore, we simply order the $(n+2)$ variables in such a way that the quantity of interest is the $(n+1)$th variable; with the $(n+2)$ variable fixed, the n remaining variables can be ordered in any one of $n!$ equivalent ways. Thus, to obtain Eq. (54), any one of the following ordering conventions applies:

$$\begin{aligned} &N_1N_2N_3SV,\\ &N_1N_3N_2SV,\\ &N_2N_1N_3SV,\\ &N_2N_3N_1SV,\\ &N_3N_1N_2SV,\\ &N_3N_2N_1SV. \end{aligned} \tag{56}$$

It is easy to verify that Eq. (53) reduces to the familiar expressions for entropy and concentration fluctuations in a single-component system:

$$\langle(\delta S)^2\rangle_V = \frac{kT_0}{(\partial T/\partial S)_{\mu,V}}, \tag{57}$$

$$\langle(\delta N)^2\rangle_V = \frac{kT_0}{(\partial\mu/\partial N)_{T,V}}. \tag{58}$$

If we define σ in terms of N, we obtain

$$\langle(\delta S)^2\rangle_N = \frac{kT_0}{(\partial T/\partial S)_{P,N}}, \tag{59}$$

$$\langle(\delta V)^2\rangle_N = \frac{-kT_0}{(\partial P/\partial V)_{T,N}}. \tag{60}$$

Equation (60) gives an expression for the fluctuations in the volume occupied by a fixed number of molecules: an operational definition will be discussed below (see the Operational Definitions section). If σ is specified by S, we have, for a single-component system,

$$\langle(\delta V)^2\rangle_S = \frac{-kT_0}{(\partial P/\partial V)_{\mu,S}}, \tag{61}$$

$$\langle(\delta N)^2\rangle_S = \frac{kT_0}{(\partial \mu/\partial N)_{P,S}}. \tag{62}$$

The denominators in Eqs. (57)–(62) are the stability coefficients for a single-component system [Eqs. (36)–(41)], as we explained in deriving Eq. (53). Thus, the vanishing of a stability coefficient and the divergence of its associated principal fluctuation are one and the same thing. As a further example, we consider binary mixtures, for which we write

$$\langle(\delta N_1)^2\rangle_V = \frac{kT_0}{(\partial \mu_1/\partial N_1)_{T,\mu_2,V}}, \tag{63}$$

$$\langle(\delta N_1)^2\rangle_S = \frac{kT_0}{(\partial \mu_1/\partial N_1)_{P,\mu_2,S}}, \tag{64}$$

$$\langle(\delta N_1)^2\rangle_{N_2} = \frac{kT_0}{(\partial \mu_1/\partial N_1)_{T,P,N_2}}, \tag{65}$$

$$\langle(\delta V)^2\rangle_{N_1} = \frac{-kT_0}{(\partial P/\partial V)_{T,\mu_2,N_1}}, \tag{66}$$

$$\langle(\delta V)^2\rangle_S = \frac{-kT_0}{(\partial P/\partial V)_{\mu_1,\mu_2,S}}, \tag{67}$$

$$\langle(\delta S)^2\rangle_{N_1} = \frac{kT_0}{(\partial T/\partial S)_{\mu_2,P,N_1}}, \tag{68}$$

$$\langle(\delta S)^2\rangle_V = \frac{kT_0}{(\partial T/\partial S)_{\mu_1,\mu_2,V}}. \tag{69}$$

Equation (65) should be compared with the expression derived by Landau and Lifshiftz[1] who write

$$\langle(\delta N_1)^2\rangle = \frac{kT_0}{(\partial \mu_1/\partial N_1)_{T,P}}.$$

It is obvious that the above equation corresponds to the constant N_2 constraint. Thus, Eq. (53) allows one to obtain expressions for principal fluctuations in a completely general way, and includes, as special cases, relationships which had, up to now, been derived on a heuristic basis.

OPERATIONAL DEFINITIONS

Having derived a general expression for principal fluctuations, we now address its operational implications.

We first consider volume fluctuations in a single-component subsystem (σ), the extent of which is specified by the number of its molecules. What is being calculated in this case is the variation in the volume occupied by N molecules. This quantity will fluctuate about a mean value, given by

$$\langle V\rangle = \frac{N}{\rho(T_0,P_0)}, \tag{70}$$

where T_0 and P_0 are the temperature and pressure of Ω.

Because we describe σ thermodynamically, we require that appropriate statistical averages be defined in σ. In particular, the distribution functions must be continuous. We consider, for convenience, μ space (a six-dimensional hyperspace), where f is defined

$$dN = f(\mathbf{r},\mathbf{v})d\mathbf{r}\, d\mathbf{v} \tag{71}$$

and we require that f be continuous. This means that dr_i $(i = 1,2,3)$ must be large compared with the average intermolecular separation, or, in other words, that the volume element $d\mathbf{r}$ must contain a large (in the thermodynamic sense) number of particles [$\mathbf{v}$ in Eq. (71) is a velocity vector].

We will determine below an appropriate size for $d\mathbf{r}$. An operational definition of volume fluctuations requires that we record the volume occupied by N molecules in units of $d\mathbf{r}$. The time dependence of this quantity will have an appearance qualitatively similar to the one exhibited by Fig. 2, from which a mean squared fluctuation can be computed.

To calculate $d\mathbf{r}$, we start by writing

$$\langle(\delta V)^2\rangle = -\frac{kT}{(\partial P/\partial V)_{T,N}} = \frac{V^2}{N}, \tag{72}$$

where the last equality is valid for ideal gases, which we consider in this example. It follows at once that

$$\frac{\langle(\delta V)^2\rangle^{1/2}}{\langle V\rangle} = \frac{1}{\sqrt{N}} \tag{73}$$

and we require that

$$\frac{d\mathbf{r}}{\langle V\rangle} \ll \frac{1}{\sqrt{N}}. \tag{74}$$

In order words, the discretization error should be small with respect to a relative fluctuation, an obvious requirement in view of the fact that we want to measure fluctuations. Again using the ideal gas law, we write, finally,

$$d\mathbf{r} \ll (kT/P)\sqrt{N}. \tag{75}$$

For $T \approx 300$ K, $P \approx 1$ bar, and $N \approx 10^{16}$ (that is, σ is, on average, a cube of 0.75 mm per side), Eq. (75) yields the criterion $d\mathbf{r} \ll 4\times10^{-12}$ cm^3. Thus, for a negligible error (say, less than 1 in 10^3), we discretize space in units of 4×10^{-15} cm^3 ($a \sim 1.6\times10^3$ Å cube), which on average, contain $\sim 10^5$ molecule each. We then have $d\mathbf{r}/\langle V\rangle \sim 10^{-11}$, but $N^{-1/2} = 10^{-8}$.

For multicomponent systems, the operational definitions of volume fluctuations which we have just discussed is also applicable to the $X_{n+2} = N_i$ constraint. In this case we simply compute the time dependence of a volume containing N_i molecules of the ith component.

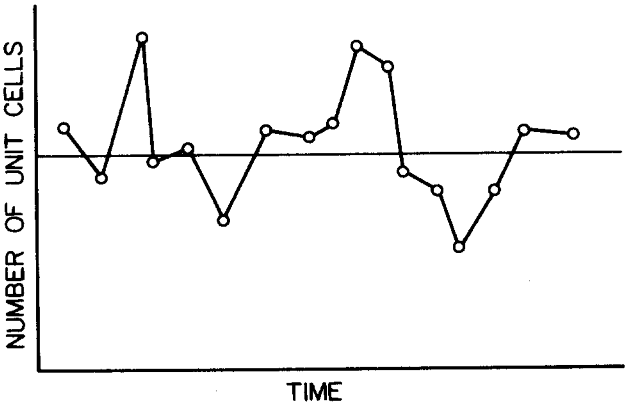

FIG. 2. Volume fluctuations within a closed system.

An operational definition for molecule number fluctuations is also easy to visualize for different choices of X_{n+2}: if σ is defined by its volume, this corresponds to concentration fluctuations, in both single and multicomponent systems. What is measured in each case is the time evolution of the number of molecules occupying a given region of space. If $X_{n+2} = N_i$, this corresponds to measuring the time evolution of the number of molecules of a given species j ($\neq i$) within boundaries which contain, at all times, N_i molecules of species i.

Whereas volume and molecule number changes can always be measured, entropy changes can be calculated but not directly measured. Thus, we calculate entropy fluctuations within a closed subsystem from measurement of the specific heat [Eq. (59)]. We can still discuss operational definitions for entropy fluctuations; as we shall see, however, the accuracy of the (hypothetical) measuring processes involved is limited *a priori* by the uncertainty relationships (which is not the case for concentration fluctuations), and the characteristics of the thought experiments are fundamentally different due to the fact that entropy (contrary to volume or mass) is not defined instantaneously.[1]

For a closed ($X_{n+2} = N$) subsystem, the operational definition of an entropy fluctuation is a thought experiment involving knowledge of the positions and momenta of the N molecules (to within the accuracy allowed by the uncertainty relationships) at a given instant, and assignment of the point representing the configuration to one of the hypercubes of volume $(\hbar')^{3N}$ into which we divide Γ space (a hyperspace with $6N$ coordinate axes, corresponding to $3N$ positions and $3N$ momenta). $\hbar'$ is a dimensionless $\hbar$ [scaled with $\lambda\,(mkT)1/2$, where λ is a characteristic length, for example, the mean free path: this allows the sides of the (dimensionless) hypercube to be of the same size, namely, $(\hbar')^{1/2}$].

The subsystem's entropy is defined only for times (τ) greater than both the position and momentum relaxation times.[1] The former corresponds to the deterministic (parabolic) portion of a mean squared displacement-vs-time curve; the latter can be taken as the duration of the interval during which a Maxwellian distribution is established following a perturbation (for example, relaxation from an initial nonequilibrium unimodal distribution). The above mentioned process is repeated over a total time $t \sim \tau$ (typically several hundred collision times), at intervals of order $\tau \hbar''/\Delta E'$, where $\Delta E'$ is a dimensionless energy uncertainty ($\beta \Delta E$), $\hbar''$ a dimensionless $\hbar$:($\hbar/\tau kT$), and $\Delta t'$, a dimensionless time, is defined in such a way that $\Delta E' = \Delta t' = (\hbar'')^{1/2}$. The logarithm of the resulting number of distinct (i.e., belonging to different elementary hypercubes) configurations is the "instantaneous" entropy, in units of k. The process is then repeated to obtain different readings of the instantaneous entropy: an entropy fluctuation can then be computed.

The implication here is that, at $t \sim \tau$, the subsystem has sampled a considerable part of the region of Γ space corresponding to the given energy, or, in other words, that the contributions associated with $t > \tau$ are small due to the fact that S is proportional to the logarithm of Γ-space volume. That this is so cannot, of course, be proved, but follows from the empirical fact that bulk properties of stochastic (irreversible, probablistic) significance, such as diffusion coefficients, are defined and measurable on the picosecond (fluid systems) time scale. That the conceptualization of an operational definition for an entropy fluctuation requires a much higher level of abstraction than is the case for concentration fluctuations is a consequence of the fact that entropy is not only not measurable, but also undefined instantaneously.

CONCLUSION

Equation (53) summarizes, in a completely general way, the relationship between principal fluctuations and stability coefficients in multicomponent systems. All Gibbs-space variable fluctuations (S, V, N_i) diverge on spinodal surfaces. The different expressions for the stability coefficients correspond univocally to fluctuations of different Gibbs-space variables, under different constaints.

The subsystem under study is always defined by specifying one (extensive) Gibbs-space variable. This gives rise to principal fluctuations which are always mathematically defined, although it is not always possible to interpret the measuring process through an operational definition.

APPENDIX A: DERIVATION OF EQ. (22)

We first write, for a generic system (σ, Ω omitted), with m any arbitrary integer

$$N^{m-1}U_{ij\ldots p} = N\frac{\partial}{\partial X_i}[N^{m-2}U_{jk\ldots p}]_{X[i]} - (m-2)N^{m-2}U_{jk\ldots p}\left(\frac{\partial N}{\partial X_i}\right)_{X[i]}, \tag{A1}$$

where $(i, j, \ldots, p)$ are m variables, and $(j, k, \ldots p)$, $m-1$ variables. Equation (A1), then, relates each term of $N^{m-1}\delta^m U$ to a term of $N^{m-2}\delta^{m-1}U$. It is easy to show that the quantity

$$N\left(\frac{\partial \alpha}{\partial X_i}\right)_{X[i]} \equiv \eta \tag{A2}$$

is always intensive, if α is intensive. Again X_i can be S, V, or any N_j ($j = 1, \ldots, n-2$). In the former case, we write

$$N\left(\frac{\partial \alpha}{\partial X_i}\right)_{X[i]} = \left(\frac{\partial \alpha}{\partial x_i}\right)_{X[i]}, \tag{A3}$$

where $x_i = X_i/N$. This is obviously an intensive quantity (if α is intensive). In the latter case,

$$N\left(\frac{\partial \alpha}{\partial X_i}\right)_{X[i]} = (1 - y_i)\left(\frac{\partial \alpha}{\partial y_i}\right)_{X[i]} \tag{A4}$$

which, again, is intensive if α is so.

Returning to Eq. (A1), we note that the derivative ($\partial N/\partial X_i$) in the right-hand side is either 0 ($X_i = S$ or V) or 1 ($X_i = N_i$). Therefore, if $N^{m-2}U_{jk\ldots p}$ is intensive, it follows that $N^{m-1}U_{ij\ldots p}$ must also be intensive. But we have shown [Eq. (18)] that NU_{ij} is intensive, so we reach the important conclusion that the quantity $N^{m-1}U_{ij\ldots p}$, where $(i, j, \ldots, p)$ are m variables, is always intensive.

To arrive at Eq. (22), we write, in Einstein notation,

$$(N^\sigma)^{m-1}\delta^m U^\sigma = (N^\sigma)^{m-1}U^\sigma_{ij\ldots p}\delta X^\sigma_i \delta X^\sigma_j \ldots \delta X^\sigma_p \tag{A5}$$

and, because Σ ($= \sigma + \Omega$) is maintained at constant, S, V,

N_i, and no chemical reaction occurs, we have

$$\delta X_i^\sigma \delta X_j^\sigma \ldots \delta X_p^\sigma = (-1)^m \delta X_i^\Omega \delta X_j^\Omega \ldots \delta X_p^\Omega. \tag{A6}$$

We now use the fact that $N^{m-1}U_{ij\ldots p}$ is intensive (and therefore equal in σ and Ω at equilibrium, about which we are expanding), and substitute Eq. (A6) into Eq. (A5), to obtain

$$(N^\sigma)^{m-1}\delta^m U^\sigma = (-1)^m (N^\Omega)^{m-1} U_{ij\ldots p}^\Omega \delta X_i^\Omega \delta X_j^\Omega \ldots \delta X_p^\Omega$$

which, in more compact form, reads

$$(N^\sigma)^{m-1}\delta^m U^\sigma = (-1)^m (N^\Omega)^{m-1}\delta^m U^\Omega. \tag{A7}$$

This is Eq. (22) and completes the proof.

APPENDIX B: CONSISTENCY

To check the thermodynamic consistency of Eq. (53), we focus our attention on a single-component system, and we define σ by the number of molecules it contains. Then Eq. (53) immediately yields

$$\langle(\delta S)^2\rangle_N = Nkc_p \tag{B1}$$

which provides a relationship to calculate entropy fluctuations in closed subsystems. We will now show how this result can be derived in a way that emphasizes the thermodynamic consistency between Eqs. (29), (30), and (53). At constant N, we have

$$dS = \frac{Nc_p}{T} dT - \left(\frac{\partial V}{\partial T}\right)_P dP, \tag{B2}$$

$$(dS)^2 = \left[N^2\left(\frac{c_p}{T}\right)^2 (dT)^2 + \left(\frac{\partial V}{\partial T}\right)_P^2 (dP)^2 - \frac{2Nc_p}{T}\left(\frac{\partial V}{\partial T}\right)_P dT\,dP\right], \tag{B3}$$

$$\langle(\delta S)^2\rangle_N = \left[N^2\left(\frac{c_p}{T}\right)^2 \langle(\delta T)^2\rangle + \left(\frac{\partial V}{\partial T}\right)_P^2 \langle(\delta P)^2\rangle - \frac{2c_pN}{T}\left(\frac{\partial V}{\partial T}\right)_P \langle\delta T\delta P\rangle\right], \tag{B4}$$

or using Eq. (29),

$$\langle(\delta S)^2\rangle_N = \left[N^2\left(\frac{c_p}{T}\right)^2 \frac{kT^2}{Nc_v} - \left(\frac{\partial V}{\partial T}\right)_P^2 (kT)\left(\frac{\partial P}{\partial V}\right)_S - \frac{2c_p}{T}\left(\frac{\partial V}{\partial T}\right)_P \frac{kT^2}{c_v}\left(\frac{\partial P}{\partial T}\right)_V\right]. \tag{B5}$$

We also know that

$$\left(\frac{\partial V}{\partial T}\right)_P\left(\frac{\partial P}{\partial T}\right)_V = -\left(\frac{\partial V}{\partial P}\right)_T\left(\frac{\partial P}{\partial T}\right)_V^2 = -\left(\frac{\partial S}{\partial P}\right)_T\left(\frac{\partial P}{\partial T}\right)_V, \tag{B6}$$

$$N\left(\frac{c_v - c_p}{T}\right) = \left(\frac{\partial V}{\partial T}\right)_P^2\left(\frac{\partial P}{\partial V}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P\left(\frac{\partial P}{\partial T}\right)_V \tag{B7}$$

which we can substitute into Eq. (B5) to obtain

$$\langle(\delta S)\rangle_N^2 = Nkc_p\left(\frac{c_p}{c_v}\right) - kT\left(\frac{\partial V}{\partial T}\right)_P^2\left(\frac{\partial P}{\partial V}\right)_S + 2Nk\left(\frac{c_p}{c_v}\right)(c_v - c_p). \tag{B8}$$

We now use the relationship

$$\left(\frac{\partial P}{\partial V}\right)_S = \left(\frac{\partial P}{\partial V}\right)_T + \left(\frac{\partial P}{\partial T}\right)_V\left(\frac{\partial T}{\partial V}\right)_S \tag{B9}$$

(constant N implied) and substitute into Eq. (B8), to obtain

$$\langle(\delta S)^2\rangle_N = Nkc_p\left(2 - \frac{c_p}{c_v}\right) - kT\left(\frac{\partial V}{\partial T}\right)_P^2\left[\left(\frac{\partial P}{\partial V}\right)_T + \left(\frac{\partial P}{\partial T}\right)_V\left(\frac{\partial T}{\partial V}\right)_S\right] \tag{B10}$$

which can be transformed, because of Eq. (B7), to read

$$\langle(\delta S)^2\rangle_N = Nkc_p\left(2 - \frac{c_p}{c_v}\right) - Nk(c_v - c_p) - kT\left(\frac{\partial V}{\partial T}\right)_P^2\left(\frac{\partial P}{\partial T}\right)_V\left(\frac{\partial T}{\partial V}\right)_S. \tag{B11}$$

We transform the last term by noting that (with constant N implied)

$$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial T}\right)_S\left(\frac{\partial T}{\partial S}\right)_V \tag{B12}$$

which implies

$$\left(\frac{\partial V}{\partial T}\right)_P^2\left(\frac{\partial P}{\partial T}\right)_V\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial V}{\partial T}\right)_P^2\left(\frac{\partial P}{\partial T}\right)_V^2\left(\frac{\partial T}{\partial S}\right)_V = -\left(\frac{cv - cp}{T}\right)^2\frac{NT}{c_v} \tag{B13}$$

or in other words,

$$\langle(\delta S)^2\rangle_N = Nkc_p\left(2 - \frac{c_p}{c_v}\right) - Nk(c_v - c_p) + \frac{Nk}{c_v}(c_v - c_p)^2 = Nkc_p \tag{B14}$$

which is identical to Eq. (B1), as it should be.

As a second consistency test, we consider the relationship

$$\langle(\delta N)^2\rangle_V = V^2\langle(\delta\rho)^2\rangle = \rho^2\langle(\delta V)^2\rangle_N \tag{B15}$$

which, in an internally consistent treatment, we should be able to derive from Eq. (53).[8] We first apply this twice, to obtain

$$\langle(\delta N)^2\rangle_V = \frac{kT_0}{\left(\frac{\partial\mu}{\partial N}\right)_{T,V}}, \tag{B16}$$

$$\langle(\delta V)^2\rangle_N = \frac{-kT_0}{\left(\frac{\partial P}{\partial V}\right)_{T,N}} \tag{B17}$$

and we must therefore have, in the light of Eq. (B15),

$$\rho^2 = -\left(\frac{\partial N}{\partial\mu}\right)_{T,V}\left(\frac{\partial P}{\partial V}\right)_{T,N}. \tag{B18}$$

To prove this, we write

$$d\mu = -s\,dT + v\,dP, \tag{B19}$$

$$\left(\frac{\partial\mu}{\partial N}\right)_{T,V} = v\left(\frac{\partial P}{\partial N}\right)_{T,V} = \frac{V}{N}\left(\frac{\partial P}{\partial N}\right)_{T,V} = -\frac{V}{N}\left(\frac{\partial P}{\partial V}\right)_{T,N}\left(\frac{\partial V}{\partial N}\right)_{T,P} = -\frac{1}{\rho^2}\left(\frac{\partial P}{\partial V}\right)_{T,N} \tag{B20}$$

which is identical to Eq. (B18): Eq. (B15) is therefore satisfied identically [the specific forms of Eq. (53) are thermodynamically consistent].

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