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Uncertainty relations of statistical mechanics

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The product of the rms fluctuations of an extensive thermodynamic variable with that of its conjugate intensive thermodynamic variable is bounded below by k in the entropy representation and by kT in the energy representation. The uncertainty relations of statistical mechanics are equivalent to the stability relations of equilibrium thermodynamics.

I. INTRODUCTION

Uncertainty relations may occur in physical theories which can be formulated in terms of canonically conjugate variables. Two well-known uncertainty relations are the position-momentum uncertainty relation $\Delta p\,\Delta q \geq \hbar/2$ of nonrelativistic quantum mechanics and the time-frequency uncertainty relation $\Delta\omega\,\Delta t \geq \frac{1}{2}$ of Fourier analysis and signal processing.

Statistical mechanics can be formulated in terms of pairs of canonically conjugate variables. We show below that uncertainty relations occur in statistical mechanics, and have the form $\Delta E^{\alpha}\Delta i_{\beta} \geq k\delta^{\alpha}{}_{\beta}$. Here E^{α} is an extensive thermodynamic variable characterizing the system, i_{β} is the intensive thermodynamic variable conjugate to E^{β} in the entropy representation, Δ represents rms fluctuations, and k is Boltzmann's constant. A similar relation holds in the energy representation, with a different set of conjugate intensive variables and k replaced by kT. We also show that the uncertainty relations of statistical mechanics are equivalent to the stability relations of equilibrium thermodynamics.

II. UNCERTAINTY RELATIONS

Consider a system $\mathscr{S}$ in thermodynamic equilibrium with a reservoir $\mathscr{R}$. The system's entropy S is a function of the system's natural extensive thermodynamic variables $E^1, E^2, \ldots, E^n$ (e.g., U,V,N, etc.). At equilibrium, the system's conjugate intensive thermodynamic variables $i_{\alpha}=\partial S/\partial E^{\alpha}$ (e.g., $1/T, P/T, -\mu/T$, etc.) are equal to the reservoir's corresponding intensive variables: $i_{\alpha}=\bar{i}_{\alpha}$.

The system will experience fluctuations around its equilibrium. Under these conditions the extensive thermodynamic variables must be considered as random variables $\hat{E}^{\alpha}$ with mean values $\overline{E^{\alpha}}=\langle \hat{E}^{\alpha}\rangle$. The probability distribution function which describes these fluctuations depends on the equilibrium state of the system (conditional probability), and is given by[1]

$$W=W(\hat{E}^{\alpha}\,|\,\bar{i}_{\beta})=\Omega_0 \exp\left[\frac{1}{k}[\hat{S}(\hat{E})-\sum \bar{i}_{\alpha}\hat{E}^{\alpha}-\bar{S}(\bar{i})]\right]. \tag{1}$$

The function $\bar{S}(\bar{i})$ is the maximum value of $\hat{S}(\hat{E})-\sum \bar{i}_{\alpha}\hat{E}^{\alpha}$; it is the Legendre transform of the equilibrium entropy.

Instead of choosing the random variables $\hat{E}$ and parameters $\bar{i}$ to define the probability distribution, it is possible to choose a dual, or conjugate, set of random variables $\hat{i}_{\alpha}$ and parameters $\bar{E}^{\beta}$ defined by

$$\hat{i}_{\alpha}=\partial\hat{S}(\hat{E})/\partial\hat{E}^{\alpha}\,, \tag{2a}$$

$$\bar{E}^{\beta}=\partial\bar{S}(\bar{i})/\partial\bar{i}_{\beta}\,. \tag{2b}$$

The parameters $\bar{i}_{\alpha}$ in (1) and $\bar{E}^{\beta}$ in (2b) are related to the random variables $\hat{i}_{\alpha}$ in (2a) and $\hat{E}^{\beta}$ in (1) by $\bar{i}_{\alpha}=\langle\hat{i}_{\alpha}\rangle$, $\bar{E}^{\beta}=\langle\hat{E}^{\beta}\rangle$.

The displacements $\delta\hat{E}^{\alpha}=\hat{E}^{\alpha}-\bar{E}^{\alpha}$ and $\delta\hat{i}_{\beta}=\hat{i}_{\beta}-\bar{i}_{\beta}$ are logarithmic derivatives of the conditional probability (1):

$$\delta\hat{E}^{\alpha}=W^{-1}\left[-k\frac{\partial}{\partial\bar{i}_{\alpha}}\right]W\,, \tag{3a}$$

$$\delta\hat{i}_{\beta}=W^{-1}\left[+k\frac{\partial}{\partial\hat{E}^{\beta}}\right]W\,. \tag{3b}$$

The second moment

$$\langle\delta\hat{E}^{\alpha}\delta\hat{i}_{\beta}\rangle=-k\delta^{\alpha}{}_{\beta} \tag{4}$$

is easily computed by integration by parts, invoking the usual boundary conditions.[1] This result has the form of an equipartition theorem for fluctuations. It also expresses the conjugacy between the extensive variables $\hat{E}$ and intensive variables $\hat{i}$.

All second moments $\langle\hat{A}\,\hat{B}\rangle$ may be regarded as inner products of vectors $\hat{A},\hat{B}$ on the linear vector space of functions defined over the space of random variables $\hat{E}^{1},\hat{E}^{2},\ldots,\hat{E}^{n}$. The measure in this inner product space is the positive definite distribution W. As a result, the Schwartz inequality may be applied to (4), yielding

$$\langle(\delta\hat{E}^{\alpha})^2\rangle^{1/2}\langle(\delta\hat{i}_{\beta})^2\rangle^{1/2}\geq|\langle\delta\hat{E}^{\alpha}\delta\hat{i}_{\beta}\rangle|$$

or

$$\Delta E^{\alpha}\Delta i_{\beta}\geq k\delta^{\alpha}_{\beta}\,. \tag{5}$$

For the pairs $(U,1/T)$, $(V,P/T)$, and $(N,-\mu/T)$ of canonically conjugate thermodynamic variables the uncertainty relations (5) take the form $\Delta U\,\Delta(1/T)\geq k$,

$\Delta V\,\Delta(P/T)\geq k$, and $\Delta N\,\Delta(\mu/T)\geq k$.

A similar calculation can be carried out in the energy representation, leading to

$$\Delta E^{\alpha}\,\Delta i'_{\beta}\geq kT\delta^{\alpha}_{\beta}\ , \tag{6}$$

where $\hat{i}'_{\beta}=\partial\hat{U}(\hat{E})/\partial\hat{E}^{\beta}$. For the pairs (S,T) $(V,-P)$, and (N,μ) of canonically conjugate variables in the energy representation, the uncertainty relations take the form $\Delta S\,\Delta T\geq kT$, $\Delta V\,\Delta P\geq kT$, and $\Delta N\,\Delta\mu\geq kT$.

III. PHYSICAL INTERPRETATION

In the canonical formulation of equilibrium statistical mechanics a system $\mathscr{S}$ is assumed to be in equilibrium with a reservoir $\mathscr{R}$ whose intensive thermodynamic variables are precisely defined. Fluctuations in the system's extensive thermodynamic variables can then be estimated as moments of the conditional probability distribution function (1).

Measurements of the system's extensive variables (e.g., U,V,N, etc.) can then be used to *estimate* the values of the intensive bath parameters (e.g., $1/T,P/T,-\mu/T$). A positive fluctuation in the system's energy ($\delta u>0$) will lead to a somewhat high estimate of the bath's temperature ($\delta T>0$). As a result, energy measurements (of $\mathscr{S}$) and temperature estimates (of $\mathscr{R}$) are positively correlated ($\delta u\,\delta T>0$). More generally, (4) describes the negative correlation between *measurements* of a system's extensive variables and *estimates* of the bath's conjugate intensive variables. The result (4) for the conjugate pair $(u,1/T)$ was derived by Gibbs [Ref. 2, Eq. (349)].[2]

Variations in measurements of the system's extensive variables $\hat{E}^{\alpha}$ are characterized by the second moments $\langle(\delta\hat{E}^{\alpha})^2\rangle$ or the square roots, ΔE^{α}. Similarly, variations in estimates of the bath's intensive variables $\bar{i}_{\alpha}$ are characterized by the second moments $\langle(\delta\hat{i}_{\alpha})^2\rangle$ or the square roots, Δi_{α}. The statistical mechanical uncertainty relations (5) and (6) are statements relating uncertainties in measurements of the system's extensive variables with uncertainties in estimates of the bath's intensive variables.

IV. DISCUSSION

The following remarks are useful.

(1) Uncertainty relations of the type (5) will occur in any physical theory formulated in terms of canonically conjugate variables which obey duality relations of the form (4), where the expectation value employs a positive (semi)definite measure.

(2) The statistical mechanical uncertainty relations are representative of a much broader class of uncertainty relations expressing the duality between probability and statistics. Typically, probability distributions for random variables (e.g., $\hat{E}^{\alpha}$) depend on parameters (e.g., $\bar{i}_{\alpha}$) whose values are fixed but unknown. Determining the probability of a measurement of random variables given the values of the parameters is the provenance of probability theory. Estimating the values of the parameters in the probability distribution given the measured values of the random variables is the provenance of statistics. Although the values of the parameters may be fixed, estimates of these values will vary because the measurements on which they are based will have varying outcomes. An uncertainty in the value of a measurement demands an uncertainty in the estimate of the parameters in the associated probability distribution.

(3) The uncertainty relations $\Delta p\,\Delta q\geq\frac{1}{2}\hbar$ and $\Delta\omega\,\Delta t\geq\frac{1}{2}$ involve a factor of $\frac{1}{2}$, not present in the statistical mechanical uncertainty relations (5) and (6). This difference comes about because the conjugacy relations in the latter case are obtained by taking derivatives of a probability distribution function, while in the former cases they are obtained from probability amplitudes

$$p\psi=\frac{\hbar}{i}\frac{\partial}{\partial x}\psi,\quad \omega f(t)=\frac{1}{i}\frac{d}{dt}f(t)$$

whose absolute square ($\psi^*(x)\psi(x)$, $f^2(t)$) is used as the probability distribution function.

(4) In the formal limits $\hbar\to 0$, $k\to 0$, quantum mechanics and statistical mechanics go over to their classical limits: classical mechanics and thermodynamics. In these limits the positive lower bounds on the uncertainty relations go to zero, indicating the lack of uncertainty relations in the classical theories.

(5) The values of the variances $\Delta E^{\alpha},\Delta i_{\beta}$ can be computed explicitly from the matrices

$$\langle\delta\hat{E}^{\alpha}\delta\hat{E}^{\beta}\rangle=-k\frac{\partial^2\bar{S}(\bar{i})}{\partial\bar{i}_{\alpha}\,\partial\bar{i}_{\beta}}=-k\bar{S}^{\alpha\beta}\ , \tag{7a}$$

$$\langle\delta\hat{i}_{\alpha}\,\delta\hat{i}_{\beta}\rangle=-k\left\langle\frac{\partial^2\hat{S}(\hat{E})}{\partial\hat{E}^{\alpha}\,\partial\hat{E}^{\beta}}\right\rangle=-k\overline{\hat{S}_{\alpha\beta}}\ . \tag{7b}$$

These matrix elements are standard thermodynamic linear response functions. The uncertainty relations take the more explicit form

$$\Delta E^{\alpha}\,\Delta i_{\alpha}=k(\bar{S}^{\alpha\alpha}\overline{\hat{S}_{\alpha\alpha}})^{1/2}\geq k\ . \tag{8}$$

The inequality $\bar{S}^{\alpha\alpha}\overline{\hat{S}_{\alpha\alpha}}\geq 1$ is a quantitative statement of LeChatelier's principle, itself a quantitative formulation of the stability criteria of equilibrium thermodynamics.[3] Therefore the uncertainty relations of statistical mechanics are equivalent to the stability relations of equilibrium thermodynamics.

(6) For a simple single component fluid the more explicit form (8) for the uncertainty relations in the energy representation is

$$\Delta S\,\Delta T=kT(C_P/C_V)^{1/2}\geq kT\ , \tag{9a}$$

$$\Delta V\,\Delta P=kT(\kappa_T/\kappa_S)^{1/2}\geq kT\ , \tag{9b}$$

where C_X are the specific heats and κ_X are the compressibilities. In the entropy representation these relations are

$$\Delta U\,\Delta(1/T)=k\left[\frac{C_P}{C_V}-\frac{2PV\alpha_P}{C_V}+\frac{P^2V\kappa_T}{TC_V}\right]^{1/2}\geq k\ , \tag{10a}$$

$$\Delta V\,\Delta(P/T)=k\left[\frac{\kappa_T}{\kappa_S}-\frac{2PV\kappa_T}{\Gamma_V}+\frac{P^2V\kappa_T}{TC_V}\right]^{1/2}\geq k\ , \tag{10b}$$

where α_P is the thermal-expansion coefficient and $\Gamma_V = T(\partial S/\partial P)_V$.

(7) Several simplifications occur in the linear-response, or Gaussian, regime. In this regime the function $\hat{S}(\hat{E})$ is expanded around the equilibrium value $\overline{\hat{E}}^{\alpha}$ and only terms up to second order in the fluctuations $\delta\hat{E}^{\alpha}$ are retained. In this regime $\bar{S}^{\alpha\beta}$ is the matrix inverse of $\overline{S_{\alpha\beta}}$: $\bar{S}^{\alpha\beta}\overline{S_{\beta\gamma}} = \delta^{\alpha}_{\gamma}$. The conjugate fluctuation quantities $\delta\hat{E}^{\alpha}, \delta\hat{i}_{\beta}$ are related by a linear susceptibility tensor: $\delta\hat{i}_{\alpha} = \overline{S_{\alpha\beta}}\,\delta\hat{E}^{\beta}$. Fluctuations about equilibrium decrease the entropy from its maximum and increase the energy from its minimum by amounts

$$\langle \delta\hat{S} \rangle = \langle \tfrac{1}{2}\overline{S_{\alpha\beta}}\delta\hat{E}^{\alpha}\delta\hat{E}^{\beta} \rangle = \tfrac{1}{2}\langle \delta\hat{i}_{\alpha}\,\delta\hat{E}^{\alpha} \rangle = -\tfrac{1}{2}nk\ , \tag{11a}$$

$$\langle \delta\hat{U} \rangle = \langle \tfrac{1}{2}\overline{U_{\alpha\beta}}\delta\hat{E}^{\alpha}\delta\hat{E}^{\beta} \rangle = \tfrac{1}{2}\langle \delta\hat{i}_{\alpha}\,\delta\hat{E}^{\alpha} \rangle = \tfrac{1}{2}nkT\ , \tag{11b}$$

where in the entropy representation

$$\delta\hat{S} = \left[\hat{S}(\hat{E}) - \sum \bar{i}_{\alpha}\hat{E}^{\alpha}\right] - \left[\hat{S}(\bar{E}) - \sum \bar{i}_{\alpha}\overline{\hat{E}^{\alpha}}\right]\ ,$$

and similarly in the energy representation. The fluctuations about these mean values are

$$\langle (\delta\hat{S})^2 \rangle - (\langle \delta\hat{S} \rangle)^2 = k\langle -\delta\hat{S} \rangle\ , \tag{12a}$$

$$\langle (\delta\hat{U})^2 \rangle - (\langle \delta\hat{U} \rangle)^2 = kT\langle \delta\hat{U} \rangle\ . \tag{12b}$$

Equations (11) are an equipartition theorem for fluctuations in entropy and energy: there is $\frac{1}{2}$ a unit $(-k, +kT)$ of potential entropy and potential energy stored in each independent thermodynamic degree of freedom. The factor $\frac{1}{2}$ is not surprising, since the Gaussian approximation is an assumption that the entropy and energy functions are quadratic forms in the displacements. Missing from this equipartition theorem is another $\frac{1}{2}$ unit of "kinetic entropy" and "kinetic energy" per thermodynamic degree of freedom associated with terms of the form

$$\sum_{\alpha,\beta} \dot{\delta\hat{E}}^{\alpha}\,\dot{\delta\hat{E}}^{\beta}\ .$$

The treatment of these kinetic terms falls outside the scope of equilibrium thermodynamics.[4]

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