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Thermodynamic Uncertainty Relations and Irreversibility

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The Cramér–Rao lower bound for the minimum variance of an unbiased estimator is derived from the second law of thermodynamics. The inequality is in the form of a uncertainty relation for conjugate thermodynamic variables where the minimum uncertainty occurs for reversible processes in which the conjugate variables are completely negatively correlated. An upper bound on the probability for arbitrarily large deviations in the energy is given in terms of the difference in entropies at the initial temperature of the body and the final equilibrium temperature of the medium.

1. INTRODUCTION

Statistical thermodynamics shares many common features with the mathematical theory of statistical inference (Mandelbrot, 1956, 1962, 1964; Lavenda and Scherer, 1987a). In fact, Boltzmann, Gibbs, and, to a greater extent, Szilard (1925) anticipated the modern theory of statistical inference as developed by Fisher (1973), Neyman and Pearson (1933), and others. The reason why statistical thermodynamics, or thermostatistics, possesses many of the properties dictated by mathematical statistics is that the distribution that maximizes the entropy, or equivalently that minimizes the "discrimination information" in the sense of Kullback and Leibler (1951), belongs to an exponential family of distributions for which means and modes coincide. However, there is an important distinction between entropy and information, apart from a sign, insofar as the prior distribution in thermostatistics is an "improper" distribution and hence not normalizable. The prior distribution, in thermostatistics, represents the degeneracy of different states with the same energy (Gibbs, 1902; Khinchin, 1949) and is responsible for the fact that the entropy, defined as the negative of the expected value

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of the logarithm of the ratio of the posterior and prior densities, has no well-defined sign, unlike that of the discrimination information (Kullback, 1959).

One of the fundamental problems in statistical inference is how to process the data concerning a random variable that are accumulated through observation beyond what is known *a priori*. An isolated system is divided into two unequal subsystems where the larger of the two acts as the thermostat. Since energy can be exchanged between the two, it is a random variable. The prior probability $\Pr(\varepsilon)$ for a state of a given energy ε in statistical mechanics is taken to be proportional to the volume of phase space that the system would occupy at that energy. Through the process of measurement, this prior probability is converted into a posterior probability $\Pr(\varepsilon|\beta)$ according to the relation

$$\Pr(\varepsilon|\beta) \propto \Pr(\beta|\varepsilon)\Pr(\varepsilon)$$

A measurement of the energy can be made with a thermometer and the estimable variable is the inverse temperature; $\Pr(\beta|\varepsilon)$ is the "likelihood" that the unknown parameter has the value β, given the datum ε. Proportionality means proportional in ε regarding β as fixed. This is analogous to Bayes' theorem (Savage, 1962), except that the roles of the "parameter" and "observable" have been interchanged. In the Bayesian case, the parameter β is considered random and it has a prior distribution that, if nothing else is known about the parameter other than that it is positive, may be taken as the logarithm uniform distribution (Lavenda, 1987).

Thermostatistics assumes that the extensive and observable quantity ε is *additive*. This means that if we take several sample systems from a population, each in contact with a thermostat with a uniform value of β, then the total value of the energy of the composite system formed from n subsystems will be n times the sample mean energy, since the interaction energy among the subsystems is assumed negligible. The additivity postulate of the energies of the subsystems plays a role analogous to the assumption that the random variables are independent and identically distributed. As the number n of independent random variables increases, the sampling variance decreases a factor of $1/n$, so that the estimate approaches its "true" value, in probability, in the limit as the number of observations increases without limit.

The analogous case in thermostatistics would be to increase the number of subdivisions of the original system in contact with the thermostat. But because of the assumed property of additivity and the macroscopic nature of the measurement, there is no gain in information from finer and finer subdivisions that could be achieved without destroying the additivity of the energy. The volume-to-surface ratio always must be large enough to warrant the assumption of additivity by neglecting the energy of interaction. If, by making finer and finer subdivisions, or, analogously, by increasing the number of observations without limit, the statistical object could be reduced to a purely mechanical one, then the entropy would reduce to zero. Consequently, thermodynamic estimators lack the asymptotic property of "consistency," since making n measurements on n subdivisions of the original system does not improve the estimate of the parameter β (Lavenda and Scherer, 1987b). Inherent in this assumption are both a lower level to the statistical description and the reproducibility of macroscopic measurements. The latter implies the smallness of thermal fluctuations at equilibrium.

The fact that the probability of a given value of the energy in any subsystem is dependent upon the sample mean energy of the subsystems and independent of the common value of β of all the subsystems means that the energy is a "sufficient" statistic for estimating β. Sufficiency in thermodynamics was first emphasized by Mandelbrot (1956, 1962). The property of sufficiency follows from the form of the posterior or Gibbs distribution; an exponential family of distributions satisfies the Fisher-Neyman factorization criterion, which essentially states that the conditional probability of observing a value of the energy of any subsystem, given the energy of the composite system, is independent of the parameter β that is to be estimated.

Thermodynamic estimators also possess the property of "unbiasedness." This property equates the *expected* value of the estimator with its true value. In fact, this is a fundamental postulate of statistical thermodynamics, which equates the expected value of an observable with the macroscopic, or thermodynamic, value of an extensive quantity.

The conjugate, or dual, variable (in the sense of a Laplace transform) can be estimated from the likelihood function $\Pr(\beta \mid \varepsilon)$, which, in contrast to the posterior distribution $\Pr(\varepsilon \mid \beta)$, is a probability distribution in the sense of "degree of belief" rather than in the "frequency" sense (Lavenda and Scherer, 1987a). In order words, there is no frequency interpretation that can be attached to opinion that certain values of β are more probable than others. $\Pr(\beta \mid \varepsilon)$, or $\Pr(\varepsilon \mid \beta)$ if we "invert" the functional dependence of the posterior distribution where the energy is now the parameter and the conjugate quantity becomes the variable (Fisher, 1973), is *not* the probability of a given value of the parameter β. As a function of β, the posterior density of the distribution $\Pr(\varepsilon \mid \beta)$ cannot be employed to compute the probability of a given value of β, but rather must be used to compare the likelihood of different values of the parameter. The fact that the maximum likelihood value of the parameter coincides with the value obtained from the first moment, in terms of the expected value of the energy, is peculiar to exponential families where means and modes coincide [cf. equation (7)] and this is responsible for the optimal properties of the statistical thermodynamic estimators. We recall that posterior densities that are exponential functions maximize the entropy and minimize discrimination information statistic.

Although the criteria of unbiasedness and sufficiency, if not consistency, apply to thermostatistic estimators, what would happen if there would be more than one candidate? Intuitively, we would feel that the better candidate would be the one with the smaller variance. It is well known that the variance of an estimator is bounded below by the Cramér-Rao (CR) lower bound (Cramér, 1946; Rao, 1945), except perhaps for a statistic which is "superefficient" having a Lebesgue measure zero (Le Cam, 1953). The CR lower bound is expressed in terms of the Fisher "information" (Fisher, 1973) and its derivation makes use of the Schwartz inequality for conjugate variables in the form that the covariance of conjugate variables cannot be greater than the product of their standard deviations. It is of no importance whether the variables are conjugate in the Fourier or Laplace sense and the resulting inequalities are the "uncertainty relations" related to the inherent limitations on the precision of physical measurements. In the Fourier case, they are the celebrated Heisenberg relations, while in the Laplace case they are the thermodynamic uncertainty relations, as first pointed out by Mandelbrot (1956).

In this article we show that (1) the CR inequality is derivable from the second law of thermodynamics, (2) minimum uncertainty occurs for reversible processes where the conjugate variables are completely negatively correlated, and (3) in a composite system composed of a medium and a small body that are not in thermal equilibrium, a bound on the probability of arbitrarily large deviations in the energy is given by the difference in the entropies calculated at the two temperatures. Consequently, as body and medium approach thermal equilibrium, the energy tends to concentrate about its average value, thereby showing the diminished importance of fluctuations in an observable variable, such as the energy, at equilibrium.

On one hand, the maximum uncertainty in the energy would therefore lead to the greatest precision possible in evaluating the temperature as would occur for an infinitely large thermostat. On the other hand, the maximum precision for measurements in the energy would occur for an isolated process in which there would be maximum uncertainty in the temperature. The former would apply to a canonical distribution, characterized by the Gibbs density, while the latter would pertain to a microcanonical distribution, described by the structure function.

For statistical decision problems in which one must decide in favor of one of two distributions, the likelihood ratio itself is considered as the relevant statistic (Wald, 1947). As far as the problem of statistical estimation is concerned, maximizing the likelihood function is usually equivalent to maximizing the likelihood ratio, since the prior distribution drops out in the maximization. In the case where there is no direct observation made on the extensive variable, the likelihood function is no longer equivalent to the likelihood ratio as far as maximum likelihood estimates are concerned (cf. Appendix). We may consider the case where the log-likelihood ratio is the statistic as the "entropy representation," as opposed to the more familiar energy representation, where the energy is the pertinent random variable.

2. LIKELIHOOD AND INDEX OF PROBABILITY

The set of all possible outcomes of measurements made upon extensive, or observable, variables $\{\varepsilon, \boldsymbol{\lambda}\}$ defines a macroscopic space Ω, where ε is the energy and $\boldsymbol{\lambda} \equiv \{\lambda_1, \ldots, \lambda_t\}$ is the vector of the external parameters of the system. According to Gibbs (1902), the structure function $p_0(\varepsilon, \boldsymbol{\lambda})$ determines the thermodynamic properties of the system. However, this prior probability density function (pdf) is "improper," since $\int p_0(\varepsilon)\, d\varepsilon$ is not finite. In the simplest case, where the energy is a quadratic definite form, the volume in phase space is proportional to the volume of an ellipsoid $(\sqrt{\varepsilon})^N$, where N is the number of degrees of freedom (Perrin, 1939). Thus, the structure function is proportional to the derivative of the phase space volume with respect to the energy, which is ε^ν, where $\nu = N/2-1$. For $N>1$, the probability that ε is less than some fixed quantity a, $\int_0^a \varepsilon^\nu\, d\varepsilon / \int_0^\infty \varepsilon^\nu\, d\varepsilon = 0$, because even though the numerator is finite, the denominator is infinite. We would therefore conclude that the probability that ε is less than any finite value is zero.

Even though the prior pdf is *improper*, the posterior pdf is a *proper* pdf. The log-likelihood ratio in Gibbs' formulation is

$$\eta = -\beta\varepsilon - \log Z(\beta) \tag{1}$$

which Gibbs (1902) called the "index of probability." The log's will refer to the natural or Naperian logarithms. Omitting the region of integration when it is the entire sample space, one has for the norming constant

$$Z(\beta) = \int e^{-\beta\varepsilon} p_0(\varepsilon)\, d\varepsilon \tag{2}$$

The Laplace transform of the structure function (2) is known as the moment generating, or "partition," function. It ensures that the posterior pdf

$$p_1(\varepsilon \,|\, \beta) = \frac{e^{-\beta\varepsilon}}{Z(\beta)} p_0(\varepsilon) \tag{3}$$

is a proper pdf and generates an exponential family of distributions, the family of the exponential type determined by $p_0(\varepsilon)$, as β ranges over its values. The exponential family is a slight generalization of the types of distributions introduced by Koopman (1936) and Pitman (1936) in their study of sufficient statistics.

Transferring our attention to the random variable η, we consider the moment generating function

$$M(\gamma)=\int e^{\gamma\eta}p_0\,d\varepsilon=\int p_1^{\gamma}p_0^{1-\gamma}\,d\varepsilon \tag{4}$$

The generating function (4) has the following properties:

(i) M is a positive and monotonically decreasing function of the parameter γ.
(ii) $M(\gamma)\to\infty$ for $\gamma\to 0$.
(iii) For any $\gamma>0$, $M(\gamma)$ has derivatives to all orders and, in particular:
(iv) $\partial^2\log M/\partial\gamma^2>0$.

We will continue to use partials to indicate that the other parameters upon the moment generating function can depend are held constant.

In an exactly analogous way that the Gibbs pdf is obtained from the structure function [cf. equation (3)] we now have the associated pdf

$$p_1(\varepsilon\,|\,\vartheta)=\frac{e^{\gamma\eta}}{M(\gamma)}p_0(\varepsilon) \tag{5}$$

with the generalized log-likelihood ratio

$$\eta^{\#}(\vartheta)\equiv\gamma\eta(\beta)-\log M=-\vartheta\varepsilon-\log Z^{\#}(\vartheta) \tag{6}$$

where the generalized partition function $Z^{\#}(\vartheta)=\int e^{-\vartheta\varepsilon}p_0(\varepsilon)\,d\varepsilon$ and only the product $\vartheta\equiv\beta\gamma$ appears. The generalized index of probability $\eta^{\#}$ reduces to Gibbs' definition (1) for the value $\gamma=1$.

The generalized index of probability $\eta^{\#}(\vartheta)$ is a concave function of the "variable" ϑ, since $Z^{\#}$ is a positive and monotonicaly decreasing function of ϑ. As $\vartheta\to 0$ and $\vartheta\to\infty$, the *negative* of the generalized index of probability tends to infinity, so that it necessarily possesses a single minimum at the point

$$-\frac{\partial\eta^{\#}}{\partial\vartheta}=\varepsilon+\frac{\partial\log Z^{\#}}{\partial\vartheta}=0 \tag{7}$$

The likelihood equation (7) is an implicit relation, which may be inverted to obtain the most likely value of $\tilde{\vartheta}=\vartheta(\bar{\varepsilon})$, where

$$\bar{\varepsilon}=-(\partial\log Z^{\#}/\partial\vartheta)_{\vartheta=\tilde{\vartheta}}$$

since $\partial^2\log Z^{\#}/\partial\vartheta^2>0$. Thus, the generalized index of probability $\eta^{\#}$ is the log-likelihood ratio in statistical inference and because the distribution is exponential, the most probable and average values coincide. Furthermore, the most likely value of the log-likelihood ratio coincides with its average value

$$\bar{\eta}^{\#}(\tilde{\vartheta}) = \int p_1^{\#}(\varepsilon \mid \tilde{\vartheta}) \log \frac{p_1^{\#}(\varepsilon \mid \tilde{\vartheta})}{p_0(\varepsilon)} \, d\varepsilon = -\tilde{\vartheta}\bar{\varepsilon} - \log Z^{\#}(\tilde{\vartheta}) \tag{8}$$

3. A MEASURE OF IRREVERSIBILITY

We now reinstate the dependences on the vector of the external parameters of the system $\boldsymbol{\lambda}$ with the intent of giving (8) a thermodynamic interpretation. The total differential of the maximum likelihood value of the generalized index of probability (8) is

$$d\bar{\eta}^{\#}(\tilde{\vartheta}) = -\tilde{\vartheta}\, d\bar{\varepsilon} - \sum_{k=1}^{r} \frac{\partial \log Z^{\#}}{\partial \lambda_k} \, d\lambda_k \tag{9}$$

due to the likelihood equation (7).

Consider a body at temperatuer T interacting with a medium at temperature T_0 and suppose, for concreteness, that $T_0 > T$. Usually, the temperature will be measured in energy units, but, where appropriate, we will convert to temperature measured in degrees by substituting $T \to k_B T$, where k_B is Boltzmann's constant. Moreover, the index "0" will be used to refer to the medium, while unindexed quantities will pertain to the body.

In addition to heat transfer from the medium to the body, an amount of work $dW = \sum_{k=1}^{r} F_k^0 \, d\lambda_k^0$ is done by the medium on the body. Whereas the forces F_k^0 represent the applied, or *observed*, values of the forces acting on the body, the values of the forces that the body is *expected* to exert are given by

$$F_k = \frac{1}{\tilde{\vartheta}} \frac{\partial \log Z^{\#}}{\partial \lambda_k} = \frac{1}{\tilde{\vartheta}} \overline{\frac{\partial \log p_0}{\partial \lambda_k}} = -\frac{\partial \bar{\varepsilon}}{\partial \lambda_k} \tag{10}$$

A derivation of this formula and a comparison with another derivation of the expected values of the forces based on the so-called principle of "adiabatic invariance" is given in the Appendix. Introducing (10) into (9) results in

$$d\bar{\eta}^{\#}(\tilde{\vartheta}) = -\tilde{\vartheta} \left\{ d\bar{\varepsilon} - \sum_{k=1}^{r} \frac{d\bar{\varepsilon}}{\partial \lambda_k} \, d\lambda_k \right\} \tag{11}$$

Now, according to the first law of thermodynamics applied to the body, the change in its average energy is given by $d\bar{\varepsilon} = dQ + \sum_{k=1}^{r} F_k^0 \, d\lambda_k^0$, where dQ is the heat given up by the medium. Due to the conservation conditions $d\lambda_k^0 = -d\lambda_k$ for each k, equation (11) can be written as

$$d\bar{\eta}^{\#}(\tilde{\vartheta}) = -\tilde{\vartheta} \left\{ dQ + \sum_{k=1}^{r} (\bar{F}_k - \bar{F}_k^0) \, d\lambda_k \right\} = -\tilde{\vartheta} T \, dS \tag{12}$$

where dS is the entropy increase of the body. Since the left-hand side is a total differential, so, too, must be the right-hand side, and this leads to the identification $\tilde{\vartheta} = 1/T$, where T is the temperature of the body.

According to the principle of global conservation of energy, $d\bar{\varepsilon} = -d\bar{\varepsilon}_0$, where $d\bar{\varepsilon}_0 = dQ_0 - \sum_{k=1}^{r} F_k^0 \, d\lambda_k^0$. Introducing this expression into equation (11) and applying the second law, we get

$$d\bar{\eta}^{\#}(\tilde{\vartheta}) = \tilde{\vartheta}\left\{dQ_0 + \sum_{k=1}^{r} (\bar{F}_k - F_k^0)\, d\lambda_k^0\right\} = \tilde{\vartheta} T_0 \, dS_0 \tag{13}$$

where dS_0 is the change in entropy of the medium. Applying the second law to the system (body + medium), $dS + dS_0 \geq 0$, we may transform equation (13) into the inequality

$$d\bar{\eta}^{\#}(\tilde{\vartheta}) \geq -\frac{T_0}{T}\, dS \tag{14}$$

But, since the left-hand side is given by equation (11), the inequality can be written as

$$d\bar{\varepsilon} - T_0\, dS + \sum_{k=1}^{r} \bar{F}_k \, d\lambda_k \leq 0 \tag{15}$$

This well-known inequality asserts that spontaneous irreversible processes occurring in the body will cause the quantity given on the left-hand side of (15) to decrease until it attains its minimum value at equilibrium. Under conditions of constant temperature (equal to the equilibrium temperature of the medium T_0) and volume (where there is only a single λ, which is the volume), it is the free energy of the body that decreases until a state of equilibrium is reached between the body and medium (Landau and Lifshitz, 1969). We will now show that the parameter γ, which is conjugate to the index of probability, characterizes a state of "disequilibrium" between the body and the medium, or, in other words, the *degree of irreversibility* of the process.

The moment generating function (4) can be written as

$$M(\gamma) = \int e^{\gamma\eta(\varepsilon)} p_0(\varepsilon)\, d\varepsilon = \int e^{(\gamma-1)\eta(\varepsilon)} p_1(\varepsilon \,|\, \beta)\, d\varepsilon \tag{16}$$

For $\gamma > 1$, the extended Chebycheff inequality (Kolmogorov, 1956) gives

$$\begin{aligned} M(\gamma) &\geq \int_{\varepsilon \leq \alpha} \exp[(\gamma-1)\eta(\varepsilon)]\, p_1(\varepsilon \,|\, \beta)\, d\varepsilon \\ &\geq \exp\{-(\gamma-1)[\beta\alpha + \log Z(\beta)]\} \Pr\{\varepsilon \leq \alpha\} \end{aligned} \tag{17}$$

Rearranging, we get

$$\Pr\{\varepsilon \leq \alpha\} \leq \exp\left[(\gamma-1)\beta\alpha + \log\frac{Z^{\#}(\vartheta)}{Z(\beta)}\right] \tag{18}$$

But this must be true for admissible values of the parameter γ, or, equivalently, for ϑ at a fixed value of β, and, in particular (Chernoff, 1952),

$$\Pr\{\varepsilon \leq \alpha\} \leq \exp[-\beta\alpha - \log Z(\beta)] \inf_{\vartheta}[\exp(\vartheta\alpha + \log Z^{\#})] \tag{19}$$

The stationary value of (19) gives

$$\alpha = -(\partial \log Z^{\#}/\partial\vartheta)_{\vartheta=\tilde{\vartheta}} = \bar{\varepsilon}$$

which turns out to be a minimum, since $Z^{\#}$ is a convex function. Consequently, inequality (19) becomes

$$\Pr\{\varepsilon \leq \bar{\varepsilon}\} \leq \exp[S(\tilde{\vartheta}) - S(\beta)] \tag{20}$$

In order that the right-hand side of (20) be a valid upper bound, it must be less than 1, which implies that $S(\beta) \geq S(\tilde{\vartheta})$. Since the entropy is necessarily a nonincreasing function of the inverse temperature, it follows that $\beta \leq \tilde{\vartheta}$. And since there are only two temperatures in the system, $T = 1/\tilde{\vartheta}$ and T_0, the latter is identified as β^{-1}. This establishes that $\gamma = T_0/T$. As $\gamma \to 1$, thermal equilibrium is established between body and medium and the energy tends to concentrate about its average value.

This conclusion can also be deduced directly from the definitions of the average generalized probability index (8), where $\bar{\eta}^{\#}(\tilde{\vartheta}) = -S(\tilde{\vartheta})$, and the average probability index

$$\bar{\eta}(\beta) = \int p_1^{\#}(\varepsilon \mid \tilde{\vartheta}) \log\frac{p_1(\varepsilon \mid \beta)}{p_0(\varepsilon)}\, d\varepsilon = -S(\beta)$$

since their difference is precisely the minimum discrimination information statistic (Kullback, 1959)

$$S(\beta) - S(\tilde{\vartheta}) = \int p_1^{\#}(\varepsilon \mid \tilde{\vartheta}) \log\frac{p_1^{\#}(\varepsilon \mid \tilde{\vartheta})}{p_1(\varepsilon \mid \beta)}\, d\varepsilon \equiv I^{\#}(\beta, \tilde{\vartheta}) \geq 0 \tag{21}$$

which follows from the inequality $x_1 \log(x_1/x_2) \geq x_1 - x_2$ and the fact that $p_1^{\#}$ and p_1 are proper pdfs.

The associated pdf $p_1^{\#}(\varepsilon \mid \tilde{\vartheta})$ minimizes the discrimination information statitic

$$I(\beta, \vartheta) = \int p_1(\varepsilon \mid \vartheta) \log\frac{p_1(\varepsilon \mid \vartheta)}{p_1(\varepsilon \mid \beta)}\, d\varepsilon$$

subject to the constraints $\int \varepsilon p_1(\varepsilon \mid \vartheta)\, d\varepsilon = \bar{\varepsilon}$ and $\int p_1(\varepsilon \mid \vartheta)\, d\varepsilon = 1$ (Kullback and Khairat, 1966). The larger the value of $I(\beta, \vartheta)$, the worse the "resemblance" between the observation and the value predicted from the ensemble with the probability density $p_1(\varepsilon \mid \beta)$. In other words, the larger the value of the discrimination information statistic, the greater is the irreversibility of the process and the larger are the deviations in the estimates of the temperature based the assumption that the observations of the energy are made on a body that is in a state of thermal equilibrium with the medium at the equilibrium temperature β^{-1}.

4. UNCERTAINTY RELATIONS AND THE CRAMER-RAO INEQUALITY

Suppose that ϑ differs slightly from a known, fixed value of β, which is the inverse of the equilibrium temperature, by the amount $\Delta\beta$. The discrimination information statistic is

$$I(\beta, \beta+\Delta\beta) = \int p_1(\varepsilon \mid \beta+\Delta\beta) \log \frac{p_1(\varepsilon \mid \beta+\Delta\beta)}{p_1(\varepsilon \mid \beta)}\, d\varepsilon \tag{22}$$

With the aid of the series expansion $\log(1+x) = x - \frac{1}{2}x^2 + o(x^2)$, the logarithm in (22) can be approximated as

$$\begin{aligned}
&\log \frac{p_1(\varepsilon \mid \beta+\Delta\beta)}{p_1(\varepsilon \mid \beta)}\\
&\quad = \log\left\{1 + \frac{p_1(\varepsilon \mid \beta+\Delta\beta) - p_1(\varepsilon \mid \beta)}{p_1(\varepsilon \mid \beta)}\right\}\\
&\quad = \frac{p_1(\varepsilon \mid \beta+\Delta\beta) - p_1(\varepsilon \mid \beta)}{p_1(\varepsilon \mid \beta)}\\
&\qquad - \frac{1}{2}\left\{\frac{p_1(\varepsilon \mid \beta+\Delta\beta) - p_1(\varepsilon \mid \beta)}{p_1(\varepsilon \mid \beta)}\right\}^2 + o[(\Delta\beta)^2]
\end{aligned}$$

Replacing the logarithm in (22) by this expression and expanding $p_1(\varepsilon \mid \beta+\Delta\beta)$ to first order in $\Delta\beta$, we obtain

$$\begin{aligned}
I(\beta, \beta+\Delta\beta) &= \frac{1}{2}\int \frac{\partial \log p_1(\varepsilon \mid \beta)}{\partial\beta} p_1(\varepsilon \mid \beta)\, d\varepsilon (\Delta\beta)^2 + o[(\Delta\beta)^2]\\
&= \frac{1}{2}\int \left(\varepsilon + \frac{\partial \log Z}{\partial \beta}\right)^2 p_1(\varepsilon \mid \beta)\, d\varepsilon (\Delta\beta)^2 + o[(\Delta\beta)^2]\\
&= \frac{1}{2}\sigma_\varepsilon^2 (\Delta\beta)^2 + o[(\Delta\beta)^2]
\end{aligned} \tag{23}$$

where σ_ε^2 is the variance in energy.

For small values of $\Delta\beta$, we have (Khinchin, 1949)

$$\Delta\varepsilon = -\frac{\partial^2 \log Z}{\partial\beta^2}\Delta\beta + o[(\Delta\beta)^2] \tag{24}$$

so that the second inequality in

$$\begin{aligned} I(\beta, \beta+\Delta\beta) &= \frac{1}{2}\sigma_\varepsilon^2(\Delta\beta)^2 + o[(\Delta\beta)^2] \\ &= \frac{1}{2}\frac{\partial^2 \log Z}{\partial\beta^2}(\Delta\beta)^2 + o[(\Delta\beta)^2] \end{aligned} \tag{25}$$

can be written as

$$\sigma_\varepsilon^2 \Delta\beta = -\Delta\varepsilon \tag{26}$$

If the medium does no work on the body (i.e., constant volume while it gives up heat to it by the amount $-Q_0 = -T_0\,\Delta S_0 = Q$, then $\Delta\varepsilon = -T_0\,\Delta S_0$. Because of the law of the increase of entropy, $\Delta S + \Delta S_0 \geq 0$, equation (26) can be written as the inequality

$$\sigma_\varepsilon^2 \Delta\beta \geq -T_0 \Delta S \tag{27}$$

At constant volume $dS = C_V\, d(\log T)$, where C_V is the heat capacity at constant volume. Provided the heat capacity is constant, the entropy change will be

$$\Delta S = C_V \log\frac{T_0 + \Delta T}{T_0} \simeq C_V \frac{\Delta T}{T_0}$$

But since $\Delta T = -T_0^2\,\Delta\beta$, inequality (27) can be cast into the suggestive form

$$\sigma_\varepsilon^2 \sigma_\beta^2 \geq 1 \tag{28}$$

where $\sigma_\beta^2 = 1/T_0^2 C_V$ is the variance of the conjugate parameter β. It is related to the mean square fluctuations in temperature by $\overline{(\Delta T)^2} = T_0^4 \sigma_\beta^2$. If T is measured in degrees, then $\sigma_\varepsilon^2 \geq k_B T_0^2 C_V$ and $\sigma_\beta^2 = k_B / T_0^2 C_V$, so that inequality (28) can be written in an analogous form to a quantum mechanical Heisenberg uncertainty relation

$$\sigma_\varepsilon \sigma_\beta \geq k_B \tag{29}$$

showing that Boltzmann's constant k_B plays the role of Planck's constant in statistical thermodynamics.

The minimum uncertainty in measurements of conjugate thermodynamic variables occurs for reversible processes for which the total entropy vanishes. If the body were isolated from the medium, the internal energy could be determined with unlimited precision at the expense of having knowledge about the temperature. Alternatively, if the medium constituted an infinite thermostat, the temperature could be determined precisely with a maximum uncertainty in the internal energy.

The uncertainty relations of thermostatistics, between conjugate (Laplace) variables, are known in mathematical statistics as the CR inequality. It provides the lower bound to the variance of the distribution in terms of the inverse of the Fisher information, which is the local form of the minimum discrimination information (23) (Kullback, 1959). An estimator having the variance of the CR lower bound is consistent, unbiased, and, since it is inversely proportional to the number of observations, its variance goes to zero as the number of observations becomes indefinitely large. In thermostatistics, we may only conclude that the variance of the CR lower bound is achieved for reversible processes, since thermostatic estimates are insensitive to the sample size or how fine the subdivisions are made. Usually, as the sample size increases without limit, what would be probable would become almost certain. Alternatively, we could imagine such a finite subdivision that the object of our investigation would no longer be statistical and, consequently, its entropy would shrink to zero.

In order to make the connection between the thermodyamic uncertainty relations and the CR lower bound more precise, suppose that $\beta(\bar{\varepsilon})$ is an unbiased estimator of β, which is obtained by solving the likelihood equation $\varepsilon+\partial(\log Z)/\partial\beta=0$. The property of unbiasedness requires

$$\int [\beta-\beta(\bar{\varepsilon})]\frac{e^{-\beta\varepsilon}}{Z(\beta)}p_0(\varepsilon)\,d\varepsilon=0 \tag{30}$$

Differentiating with respect to β gives

$$1+\int [\beta-\beta(\bar{\varepsilon})](\varepsilon-\bar{\varepsilon})\frac{e^{-\beta\varepsilon}}{Z(\beta)}\,d\varepsilon\equiv 1+\operatorname{cov}(\beta,\varepsilon)=0 \tag{31}$$

The correlation coefficient ρ is defined as the ratio $\rho=\operatorname{cov}(\beta,\varepsilon)/\sigma_\varepsilon\sigma_\beta$ and since the covariance $\operatorname{cov}(\beta,\varepsilon)$ is negative, ρ is negative, implying negative correlations between the conjugate variables ε and β. Furthermore, since $|\rho|\leq 1$, we get $\sigma_\varepsilon\sigma_\beta\geq 1$ for temperatures that are measured in energy units. We have derived the same inequality from the second law, which provides a physical interpretation of the CR lower bound.

The statistical efficiency of the unbiased estimator is defined as

$$\operatorname{eff}(\beta(\bar{\varepsilon}))=\{\sigma_\beta\sigma_\varepsilon\}^{-2}$$

Maximum efficiency occurs when the conjugate variables are completely *negatively* correlated (i.e., $\rho=-1$) and this implies a perfect linear *negative* relationship between the variables. The values of ρ on the closed interval $[-1, 0]$ can be used as a measure of the degree of correlation between the conjugate variables and provide some valuable insight into the modification that the equations of state must incur as the system moves away from thermodynamic equilibrium. The lack of linear correlations between β and ε can be deduced from the value $\rho = 0$, but it cannot be concluded that the variables are statistically independent, while the converse is true.

The CR lower bound is inversely proportional to the number of observations, so that any estimator having this variance will be asymptoticaly consistent as the number of observations becomes indefinitely large. In thermostatistics, the asymptotic values of the variance is approached in the limit of a *reversible* process and will always remain finite, since there is no inverse dependence on the number of observations or the number of subdivisions of the original system.

There is a definite similarity between uncertainty relations and measurements in quantum mechanics and thermostatistics. Consider the uncertainty relation between momentum and position. Momentum may be "estimated" from measurements of position by a time-of-flight technique (Feynman and Hibbs, 1965). The error in the momentum is proportional to the uncertainty in the initial position of the particle. The error in determining the initial position of the particle would be analogous to the standard deviation of the sample mean energy and the estimate of the momentum in terms of position measurements corresponds to the estimation of the temperature from observations made on the energy.

APPENDIX

According to the principle of "adiabatic invariance" the *a priori* probability "must always depend on those quantities which remain invariant under adiabatic influencing."[2] An adiabatic process requires that the change in the external coordinates be slow that at any instant the body may be regarded as being in a state of equilibrium. The fact that $\partial S/\partial\lambda_k \, \alpha \, \dot{\lambda}_k$ implies that an adiabatic process is also a reversible process, since when $\dot{\lambda}_k \to 0$, so does $dS/d\lambda_k$ (Landau and Lifshitz, 1969). However, since an adiabatic process requires the entropy of each subsystem of the composite system to be constant, rather than requiring that the total entropy of the system be constant, not every reversible process is an adiabatic process.

Khinchin (1949) and, more emphatically, Mandelbrot (1964) have claimed that in order for the quantity $\oint \beta \, dQ$, calculated over a cycle, to be path-independent it is sufficient that

$$-\beta \int \left(\frac{\partial \varepsilon}{\partial \lambda_k}\right) e^{-\beta\varepsilon} p_0(\varepsilon, \boldsymbol{\lambda}) \, d\varepsilon = \frac{\partial Z(\beta, \boldsymbol{\lambda})}{\partial \lambda_k} \qquad \text{(A1)}$$

In order for condition (A1) to hold, it is necessary that $\overline{\partial \log p_0/}\partial \lambda_k = 0$.

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[2] Paul Ehrenfest in a letter to A. F. Joffe (see Klein, 1985, p. 261).

As far as the estimation of the parameter β was concerned, it was immaterial whether we considered the log-likelihood ratio, $\log[p_1(\varepsilon\,|\,\beta)/p_0(\varepsilon)]$, or the log-likelihood function, $\log p_1(\varepsilon\,|\,\beta)$, since the two differ by a constant factor, which cancels out in the maximization. However, if the expected values of the forces are to be estimated, then the two log-likelihoods cannot be used interchangeably.

We now show that equation (10) is, in fact, correct by using what Lorentz (1916) called "la remarquable insensibilité de la formula de Boltzmann," insofar as the Boltzmann and Gibbs definitions of entropy essentially coincide for a system in equilibrium. According to Boltzmann, the definition of temperature is

$$\tilde{\beta} = \beta(\bar{\varepsilon}) = (\partial \log p_0/\partial \varepsilon)_{\varepsilon=\bar{\varepsilon}}$$

and expected forces are

$$\bar{F}_k = -\tilde{\beta}^{-1}\,\partial \log p_0(\bar{\varepsilon}, \boldsymbol{\lambda})/\partial \lambda_k.$$

These are precisely the maximum likelihood estimates that render the log-likelihood function $\log p_1(\varepsilon\,|\,\beta, \boldsymbol{\lambda})$ an extremum.

The total differential of the log-likelihood function is

$$\begin{aligned} d \log p_1(\varepsilon\,|\,\beta, \boldsymbol{\lambda}) &= -\varepsilon\, d\beta - \beta\, d\varepsilon - \frac{\partial \log Z}{\partial \beta}\, d\beta - \sum_{k=1}^{r} \frac{\partial \log Z}{\partial \lambda_k}\, d\lambda_k \\ &\quad + \frac{\partial \log p_0}{\partial \varepsilon}\, d\varepsilon + \sum_{k=1}^{r} \frac{\partial \log p_0}{\partial \lambda_k}\, d\lambda_k \end{aligned} \tag{A2}$$

Evaluating (A2) at the maximum likelihood value

$$\bar{\varepsilon} = -(\partial \log Z/\partial \beta)_{\beta=\tilde{\beta}}$$

yields

$$\begin{aligned} d \log p_1(\bar{\varepsilon}\,|\,\tilde{\beta}, \boldsymbol{\lambda}) &= -\left[\tilde{\beta} - \left(\frac{\partial \log p_0}{\partial \varepsilon}\right)_{\varepsilon=\bar{\varepsilon}}\right] d\bar{\varepsilon} - \sum_{k=1}^{r} \left(\tilde{\beta}\bar{F}_k - \frac{\partial \log p_0}{\partial \lambda_k}\right) d\lambda_k \end{aligned} \tag{A3}$$

The condition for an extremum, $d \log p_1(\bar{\varepsilon}\,|\,\tilde{\beta}, \boldsymbol{\lambda}) = 0$, is satisfied by requiring the terms in the parentheses to vanish; this yields the Boltzmann definition of temperature and expected external forces. The maximum likelihood estimates and their average values coincide precisely because they have been obtained from an exponential family of distributions. Furthermore, the Gibbs and Boltzmann definitions of entropy coincide, namely

$$-d\bar{\eta} = d \log p_0(\bar{\varepsilon}, \boldsymbol{\lambda})$$

due to the extremum condition of the log-likelihood function, $d \log p_1(\bar{\varepsilon} \mid \tilde{\beta}, \boldsymbol{\lambda}) = 0$. This is in full support of Lorentz's statement about the remarkable insensitivity of the Boltzmann definition of entropy at equilibrium.

It is somewhat curious that both derivations can be found in Gibbs (1902) without any mention of the principle of adiabatic invariance. In the first case, he considers

$$e^{-\beta\Psi} = \int \cdots \int e^{-\beta\varepsilon}\, dp_1 \cdots dq_n \tag{A4}$$

where the integrals extend over all phases in phase space and Ψ is the Helmholtz free energy. Assuming the external coordinates to be "contained implicitly in ε," he compared the total differential of (A4) with the thermodynamic relation

$$d\Psi = -\beta^{-2}\bar{\eta}\, d\beta + \sum_{k=1}^{r} (\partial\bar{\varepsilon}/\partial\lambda_k)\, d\lambda_k$$

to obtain $\partial\bar{\varepsilon}/\partial\lambda_k = -\bar{F}_k$.

In the second case, Gibbs considered

$$e^{-\beta\Psi} = \int e^{-\beta\varepsilon+\phi}\, d\varepsilon \tag{A5}$$

where the external coordinates are "contained implicitly in ϕ," which in our notation stands for $\log p_0$. A comparison of the total differential of (A5) with the thermodynamic relation now gives $\overline{\partial\phi/\partial\lambda_k} = \beta\bar{F}_k$.

The first derivation implies a certain "conditioning" of the random variable ε upon the external coordinates. Actually, it is not the random variable itself that is a function of the external coordinates, but rather its average value, which is defined thermodynamically. Such a conditioning of a random variable is completely foreign to mathematical statistics and the method of maximum likelihood indicates that the correct procedure is to consider the prior density p_0 to be a function of the external coordinates rather than the random variable itself.

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