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Continuity of the Temperature and Derivation of the Gibbs Canonical Distribution in Classical Statistical Mechanics

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For a classical system of interacting particles we prove, in the microcanonical ensemble formalism of statistical mechanics, that the thermodynamic-limit entropy density is a differentiable function of the energy density and that its derivative, the thermodynamic-limit inverse temperature, is a continuous function of the energy density. We also prove that the inverse temperature of a finite system approaches the thermodynamic-limit inverse temperature as the volume of the system increases indefinitely. Finally, we show that the probability distribution for a system of fixed size in thermal contact with a large system approaches the Gibbs canonical distribution as the size of the large system increases indefinitely, if the composite system is distributed microcanonically.

KEY WORDS: Foundations of statistical mechanics; continuity of the temperature; Gibbs canonical distribution.

1. INTRODUCTION

For any system in statistical mechanics, experience leads us to believe that the temperature is a continuous function of the energy. That is, we expect that no matter how simple or complicated a system may be, its thermodynamic behavior will be such that no "phase transition" will occur in which the temperature changes abruptly. In this paper we give a rigorous proof that for a classical system of particles the thermodynamic-limit entropy density is a differentiable function of the energy density and that its derivative, the thermodynamic-limit inverse temperature, is a continuous function of the

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energy density. We also prove that the inverse temperature of a finite system approaches the thermodynamic-limit inverse temperature as the volume of the finite system increases indefinitely. As a corollary, we show that the probability distribution of a small system in thermal contact with a large one approaches the Gibbs canonical distribution as the large system increases indefinitely, if the composite system is distributed microcanonically.

The proofs follow from the properties of convex functions. In particular, the continuity of the thermodynamic-limit inverse temperature as a function of the energy density follows from the concavity of the thermodynamic-limit entropy density and the convexity in the energy density of a certain monotonic function of the thermodynamic-limit entropy density. The convexity of this function is established with the help of the Schwarz inequality. The only assumptions needed for these results are the stability and temperedness of the potential (Ref. 1, pp. 32–33).

2. DEFINITIONS

We consider a system of n identical particles of mass m enclosed in a ν-dimensional container Λ with total energy E. The microcanonical partition function Ω_Λ is defined by

$$\Omega_\Lambda(E, n) = (n!)^{-1} \int_{\Lambda^n} d\mathbf{x} \int_{R^{n\nu}} d\mathbf{p}\, \delta^+[E - H(\mathbf{x}, \mathbf{p})] \tag{1}$$

where $(\mathbf{x}, \mathbf{p}) = (x_1,..., x_n, p_1,..., p_n)$, $d\mathbf{x} = dx_1 \cdots dx_n$, $d\mathbf{p} = dp_1 \cdots dp_n$, with $x_i \in \Lambda$, $p_i \in R^\nu$. The symbols x_i and p_i, respectively, denote the position and momentum vectors of the ith particle. The symbol δ^+ denotes the unit step function defined by $\delta^+(t) = 1$ for $t > 0$ and $\delta^+(t) = 0$ for $t < 0$. The function H is the Hamiltonian of the system defined by

$$H(\mathbf{x}, \mathbf{p}) = (2m)^{-1} \sum_{i=1}^{n} p_i^2 + U(\mathbf{x})$$

where U denotes the potential energy.

Let $E_\Lambda^{(0)}$ denote the infimum of the potential U for $\mathbf{x} \in \Lambda^n$, which exists since the potential U is stable. Then, if $E > E_\Lambda^{(0)}$, we define the entropy S_Λ, taking units where Boltzmann's constant is 1, by

$$S_\Lambda(E, n) = \log \Omega_\Lambda(E, n) \tag{2}$$

The entropy density s_Λ, which is a function of the energy density ϵ and the number density ρ, is defined by

$$s_\Lambda(\epsilon, \rho) = V^{-1}(\Lambda) S_\Lambda(E, n) \tag{3}$$

where $\epsilon = E/V(\Lambda)$ and $\rho = n/V(\Lambda)$ and $V(\Lambda)$ denotes the volume of the container Λ.

For $\epsilon > \epsilon_\Lambda^{(0)}$, with $\epsilon_\Lambda^{(0)} = E_\Lambda^{(0)}/V(\Lambda)$, the inverse temperature β_Λ is defined by

$$\beta_\Lambda(\epsilon, \rho) = \partial s_\Lambda(\epsilon, \rho)/\partial\epsilon = \Omega_\Lambda'(E, n)/\Omega_\Lambda(E, n) \tag{4}$$

where Ω_Λ' denotes the partial derivative of Ω_Λ with respect to E.

For stable tempered potentials, the thermodynamic-limit entropy density is defined by

$$s(\epsilon, \rho) = \lim_{\Lambda\to\infty} s_\Lambda(\epsilon_\Lambda, \rho_\Lambda) \tag{5}$$

where $\{\epsilon_\Lambda\}$ and $\{\rho_\Lambda\}$ are sequences which approach ϵ and ρ as Λ increases indefinitely in the sense of Fisher. The existence of the limit in (5) is proved by Ruelle (Ref. 1, Chapter 3), provided that (ϵ, ρ) lies on a certain convex set θ (whose exact definition is not important for our purposes).

The thermodynamic-limit entropy density is a concave function of ϵ (Ref. 1, Chapter 3). Hence (Ref. 2, p. 5), the left- and right-hand partial derivatives with respect to ϵ exist for all $(\epsilon, \rho) \in \theta$. Denoting these derivatives by β_- and β_+, respectively, they must satisfy the inequality

$$\beta_+(\epsilon, \rho) \leqslant \beta_-(\epsilon, \rho) \tag{6}$$

Wherever the left and right derivatives of s with respect to ϵ coincide they are continuous (Ref. 2, p. 7) and we define the thermodynamic-limit inverse temperature β as this common value.

3. CONTINUITY OF THE TEMPERATURE

We start by proving that in the microcanonical ensemble formalism the thermodynamic-limit entropy density s is a differentiable function of the energy density and that the thermodynamic-limit inverse temperature β is continuous in the energy density ϵ. The proof follows from the concavity of s and the convexity in ϵ of a function σ related to s by Eq. (11) below. Next, we prove that the inverse temperature of a finite system approaches the thermodynamic-limit inverse temperature as the volume of the finite system increases indefinitely.

If we integrate Eq. (1) with respect to the momenta, we find that

$$\Omega_\Lambda(E, n) = \frac{(2\pi m)^{n\nu/2}}{n!\,\Gamma(n\nu/2 + 1)} \int_{\Lambda^n} d\mathbf{x}\, [E - U(\mathbf{x})]^{n\nu/2}\, \delta^+[E - U(\mathbf{x})] \tag{7}$$

where Γ denotes the gamma function. On the other hand, from Eq. (4) we note that

$$\frac{\partial\beta_\Lambda(\epsilon, \rho)}{\partial\epsilon} = V(\Lambda)\beta_\Lambda^2(\epsilon, \rho)\left\{\frac{\Omega_\Lambda(E, n)\Omega_\Lambda''(E, n)}{[\Omega_\Lambda'(E, n)]^2} - 1\right\} \tag{8}$$

where Ω_Λ'' denotes the partial derivative of Ω_Λ' with respect to E. By differentiating formula (7) we can obtain integral formulas for $\Omega_\Lambda'(E, n)$ and $\Omega_\Lambda''(E, n)$. These integrals are related, if $n\nu/2 \geqslant 2$, by the Schwarz inequality

$$\left\{\int_{\Lambda^n} d\mathbf{x}\,[E - U(\mathbf{x})]^{n\nu/2-1}\,\delta^+[E - U(\mathbf{x})]\right\}^2$$

$$\leqslant \int_{\Lambda^n} d\mathbf{x}\,[E - U(\mathbf{x})]^{n\nu/2}\,\delta^+[E - U(\mathbf{x})]$$

$$\times \int_{\Lambda^n} d\mathbf{x}\,[E - U(\mathbf{x})]^{n\nu/2-2}\,\delta^+[E - U(\mathbf{x})]$$

From this inequality and Eq. (7) we obtain

$$\frac{\Omega_\Lambda(E, n)\Omega_\Lambda''(E, n)}{[\Omega_\Lambda'(E, n)]^2} \geqslant 1 - \frac{2}{n\nu}$$

Using this in Eq. (8), we find that

$$\frac{\partial \beta_\Lambda(\epsilon, \rho)}{\partial \epsilon} + \frac{2}{\nu\rho}\,\beta_\Lambda{}^2(\epsilon, \rho) \geqslant 0 \tag{9}$$

Now, let σ_Λ be the function defined by

$$\sigma_\Lambda(\epsilon, \rho) = \exp[(2/\nu\rho)s_\Lambda(\epsilon, \rho)] \tag{10}$$

Then

$$\frac{\partial^2 \sigma_\Lambda(\epsilon, \rho)}{\partial \epsilon^2} = \frac{2}{\nu\rho}\,\sigma_\Lambda(\epsilon, \rho)\left[\frac{\partial \beta_\Lambda(\epsilon, \rho)}{\partial \epsilon} + \frac{2}{\nu\rho}\,\beta_\Lambda{}^2(\epsilon, \rho)\right]$$

From this expression and inequality (9) it follows that σ_Λ is convex in ϵ. Let σ be the thermodynamic limit of σ_Λ, which exists in view of Eq. (5). That is,

$$\sigma(\epsilon, \rho) = \lim_{\Lambda\to\infty} \sigma_\Lambda(\epsilon, \rho) = \exp[(2/\nu\rho)s(\epsilon, \rho)] \tag{11}$$

The function σ is convex in ϵ since it is the limit of a sequence of convex functions (Ref. 2, p. 17). Hence, its left- and right-hand derivatives with respect to ϵ, which we denote by $\partial\sigma/\partial\epsilon_-$ and $\partial\sigma/\partial\epsilon_+$, respectively, exist, are continuous except, at most, on a countable number of points, and satisfy the inequality

$$\partial\sigma(\epsilon, \rho)/\partial\epsilon_- \leqslant \partial\sigma(\epsilon, \rho)/\partial\epsilon_+$$

By Eq. (11) this implies that

$$\beta_-(\epsilon, \rho) \leqslant \beta_+(\epsilon, \rho) \tag{12}$$

From inequalities (6) and (12) it follows that $\beta_- = \beta_+$ for all ϵ and hence that the thermodynamic-limit entropy density s is a differentiable function of ϵ and that its derivative, the thermodynamic-limit inverse temperature β, is continuous in ϵ.

There is a theorem on convex functions (Ref. 2, p. 20; Ref. 3), which states that if a sequence of differentiable convex functions has a limit, then the sequence of derivatives converges to the derivative of the limit function at the points where the latter is continuous. Applying this theorem to the sequence of functions σ_Λ, we have

$$\lim_{\Lambda\to\infty} \partial\sigma_\Lambda(\epsilon, \rho)/\partial\epsilon = \partial\sigma(\epsilon, \rho)/\partial\epsilon$$

since $\partial\sigma(\epsilon, \rho)/\partial\epsilon$ is continuous in ϵ. This result may also be written

$$\lim_{\Lambda\to\infty} \beta_\Lambda(\epsilon, \rho) = \beta(\epsilon, \rho) \tag{13}$$

4. DERIVATION OF THE CANONICAL DISTRIBUTION

To prove that a finite system in thermal contact with an infinite heat bath is distributed canonically, we first use the above results to show that in the thermodynamic limit

$$\lim_{\Lambda\to\infty} \frac{\Omega_\Lambda(E - \Delta E, n)}{\Omega_\Lambda(E, n)} = \exp[-\Delta E\beta(\epsilon, \rho)] \tag{14}$$

whenever $E/V(\Lambda) \to \epsilon$, $n/V(\Lambda) \to \rho$ with $(\epsilon, \rho) \in \theta$ as Λ increases indefinitely in the sense of Fisher, and $\Delta E \geqslant 0$ is arbitrary and does not depend on Λ.

Let us define $\Delta\epsilon = \Delta E/V(\Lambda) = \Delta E\rho/n$, where $\Delta\epsilon \geqslant 0$. Since σ_Λ is convex in ϵ, we have

$$\sigma_\Lambda(\epsilon \pm \Delta\epsilon, \rho) \geqslant \sigma_\Lambda(\epsilon, \rho) \pm (2\Delta\epsilon/\nu\rho)\sigma_\Lambda(\epsilon, \rho)\beta_\Lambda(\epsilon, \rho) \tag{15}$$

Using Eqs. (2), (3), (10), and (15) we may write

$$\begin{aligned}
\frac{\Omega_\Lambda(E \pm \Delta E, n)}{\Omega_\Lambda(E, n)} &= \left[\frac{\sigma_\Lambda(\epsilon \pm \Delta\epsilon, \rho)}{\sigma_\Lambda(\epsilon, \rho)}\right]^{n\nu/2} \\
&\geqslant \left[1 \pm \frac{2\Delta\epsilon}{\nu\rho}\beta_\Lambda(\epsilon, \rho)\right]^{n\nu/2} \\
&= \exp\left\{-\frac{n\nu}{2}\log\left[1 \mp \frac{(2\Delta\epsilon/\nu\rho)\beta_\Lambda(\epsilon, \rho)}{1 \pm (2\Delta\epsilon/\nu\rho)\beta_\Lambda(\epsilon, \rho)}\right]\right\} \\
&\geqslant \exp\frac{\pm\Delta E\beta_\Lambda(\epsilon, \rho)}{1 \pm (2\Delta\epsilon/\nu\rho)\beta_\Lambda(\epsilon, \rho)}
\end{aligned} \tag{16}$$

where we have used the fact that $\log(1 + x) \leqslant x$. For the case of the plus sign in (16), we replace E by $E - \Delta E$ to obtain

$$\exp \frac{-\Delta E \beta_\Lambda(\epsilon, \rho)}{1 - (2\Delta\epsilon/\nu\rho)\beta_\Lambda(\epsilon, \rho)} \leqslant \frac{\Omega_\Lambda(E - \Delta E, n)}{\Omega_\Lambda(E, n)}$$

$$\leqslant \exp \frac{-\Delta E \beta_\Lambda(\epsilon - \Delta\epsilon, \rho)}{1 + (2\Delta\epsilon/\nu\rho)\beta_\Lambda(\epsilon - \Delta\epsilon, \rho)}$$

Finally, letting Λ grow indefinitely, (14) follows, since β is continuous in ϵ.

We now consider a finite system $\mathscr{S}^{(1)}$, whose Hamiltonian we denote by $H^{(1)}$, in thermal contact with a system $\mathscr{S}^{(2)}$ enclosed in a finite container Λ, which we call the heat bath. (By "thermal contact" we mean that there is an interaction between $\mathscr{S}^{(1)}$ and $\mathscr{S}^{(2)}$ strong enough to bring the composite system to equilibrium but not strong enough to affect the total energy appreciably.) We want to find the probability distribution for $\mathscr{S}^{(1)}$, when the composite system is distributed microcanonically and $\mathscr{S}^{(2)}$ grows indefinitely while $\mathscr{S}^{(1)}$ remains unchanged. We know[6] that the probability density $\mu_\Lambda^{(1)}$ on the phase space of $\mathscr{S}^{(1)}$ is given by

$$\mu_\Lambda^{(1)}(\mathbf{x}, \mathbf{p}) = C_\Lambda \Omega_\Lambda(E_\Lambda - H^{(1)}(\mathbf{x}, \mathbf{p}), n)$$

where now $(\mathbf{x}, \mathbf{p})$ denotes a point in the phase space of $\mathscr{S}^{(1)}$, C_Λ is a normalizing constant given by

$$C_\Lambda = \left[\int d\mathbf{x} \int d\mathbf{p}\, \Omega_\Lambda(E - H^{(1)}(\mathbf{x}, \mathbf{p}), n)\right]^{-1}$$

and the integration is carried out over the phase space of $\mathscr{S}^{(1)}$. With the help of (14) we then find that

$$\lim_{\Lambda \to \infty} \mu_\Lambda^{(1)}(\mathbf{x}, \mathbf{p}) = \frac{\exp[-\beta(\epsilon, \rho) H^{(1)}(\mathbf{x}, \mathbf{p})]}{\int d\mathbf{x} \int d\mathbf{p} \exp[-\beta(\epsilon, \rho) H^{(1)}(\mathbf{x}, \mathbf{p})]} \tag{17}$$

This shows that the probability distribution for a small system in thermal contact with an infinitely large heat bath is the Gibbs canonical distribution.

5. CONCLUSIONS

We have proved that in the microcanonical ensemble formalism of classical statistical mechanics the thermodynamic-limit entropy density is a differentiable function of the energy density and that its derivative, the thermodynamic-limit inverse temperature, is continuous in the energy density. We have also proved that the inverse temperature of a finite system approaches the thermodynamic-limit inverse temperature as the volume of the system increases indefinitely. Finally, we proved that the probability distribution for a finite, classical system in thermal contact with an infinite heat bath, the composite system being distributed microcanonically, is the Gibbs canonical distribution.

One of the aims of equilibrium statistical mechanics is to establish sufficient conditions on the microscopic interactions in a system composed of a great number of particles, in order that the system exhibit thermodynamic behavior. That is, we would like to be able to prove, for suitable systems, that the postulates of thermodynamics apply in the thermodynamic limit. In Callen's[5] postulational approach to thermodynamics, one of the postulates is that the entropy density is a continuous and differentiable function of the energy density. Our result shows that Callen's postulate applies to classical systems of particles with stable and tempered potentials.

There has been some previous work on the problems considered in this paper. The canonical distribution formula (17) for the case where the heat bath is an ideal monatomic classical gas goes back to Maxwell.[4] For the case where the heat bath consists of a large number of identical noninteracting classical components of arbitrary structure, the result was proved by Khinchin.[6] Mazur and Van der Linden[7] extended Khinchin's proof to systems of particles interacting by potentials of a special type (square well interaction). They assumed that β is not a limit point of complex zeros of the canonical partition function, so that their result does not apply at the temperature of a phase transition.

In a later paper[8] Van der Linden considered the related problem of proving that the thermodynamic limit of the inverse temperature exists and is equal to the thermodynamic-limit inverse temperature [Eq. (13) above]. His proof, which is quite complicated, starts from inequality (9) and applies to any stable and tempered potential. Like ours, his proof depends on the continuity of the thermodynamic-limit inverse temperature. In his paper, this continuity is proved by using the thermodynamic equivalence of the microcanonical and canonical ensembles, whereas we are able to avoid appealing to this equivalence.

The problem of proving that the thermodynamic-limit temperature is continuous can also be considered in its own right. As commented by Griffiths and by Lieb,[9] once the thermodynamic equivalence of the microcanonical and canonical ensembles is established, the continuity of the thermodynamic-limit temperature follows from the fact that this continuity is equivalent to strict convexity of the function f defined by

$$f(\beta, \rho) = \sup_{\epsilon} [s(\epsilon, \rho) - \beta\epsilon]$$

In turn, this strict convexity property can be established from the fact that the canonical partition function factors into a product of configurational and kinetic parts, the first being at least log-convex and the second strictly log-convex.

There appears to be no difficulty in generalizing our results to other types of classical systems with kinetic degrees of freedom, but it still remains to be seen if the results hold in the quantum mechanical case.

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NOTE ADDED IN PROOF

The argument given to justify (14) is incomplete. Continuity of β in ϵ is not enough; we also need uniform convergence in ϵ of the sequence of functions β_Λ. This uniformity follows from the uniform convergence of the sequence of functions $\partial\sigma_\Lambda/\partial\epsilon$, which in turn follows from the convexity of σ_Λ in ϵ and the continuity of $\partial\sigma/\partial\epsilon$.

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