Proof of the Third Law of Thermodynamics for Ising Ferromagnets

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The third law of thermodynamics is proved for a large class of Ising models with generalized ferromagnetic many-body interactions. A sufficient condition for the third law to hold is that the model have nearest-neighbor couplings which are bounded from below by a positive constant. The proof is based on a spin-correlation inequality of Griffiths which implies a corresponding inequality for the bulk entropy per spin. Ground-state degeneracy considerations are completely avoided.

The third law of thermodynamics (TLT), originally conceived by Nernst in order to predict the equilibrium conditions of chemical reactions, has since become recognized as a fundamental principle of physics and chemistry.[1] Its theoretical foundations lie in the domain of quantum-statistical mechanics, and it has been shown to be satisfied for a number of specific soluble model systems. However, statements concerning its validity for classes of systems whose Hamiltonians have certain general properties, and which may not be soluble at present, have been few.[2–5]

In this paper, we prove that TLT is obeyed by a large class of Ising models with generalized ferromagnetic many-body interactions. The proof makes use of an inequality of Griffiths,[6–8] which has already been useful in a rigorous proof that the three-dimensional Ising model exhibits long-range order for sufficiently small positive temperatures. This inequality and others related to it have been the focus of considerable recent discussion because of their applications to Ising systems and their potential extensions to other types of systems.[8] It is perhaps surprising that one of these inequalities allows an elementary and very general proof of TLT.

A simple statement of TLT is that the zero-temperature limit of the *bulk* thermodynamic entropy per particle exists, and is independent of all external parameters. For the Ising models considered here, there is but one such parameter, the external magnetic field. The adopted statement of the third law entails taking the thermodynamic limit *before* the zero-temperature limit, a point of view which has been explained in some detail by Griffiths,[9] and which is in accord with the modern-day philosophy of "rigorous" statistical mechanics. In particular, it avoids any explicit discussion of ground-state degeneracy and, consequently, is not subject to the various criticisms[2,3,5,9] which have been leveled at that type of approach.

Consider an Ising lattice, which consists of a set Λ of N spins in some geometric configuration in one, two, or three dimensions. To the ith spin, assign the quantum number σ_i which is $+1(-1)$ when the spin is up (down). Let R represent a subset of Λ and define

$$\sigma_R = \prod_{i\in R} \sigma_i \, . \tag{1}$$

For each set R, let $J(R) \geq 0$ represent the corresponding many-body coupling constant. When R consists of a single site, say i, $J(i) \equiv \mu H$, where μ is a magnetic moment and $H \geq 0$ is a uniform external magnetic field. The system's Hamiltonian is taken to be

$$\mathcal{H} = -\sum_R J(R)\, \sigma_R \, . \tag{2}$$

The sum runs over all subsets R of Λ. If the system is at temperature $T=(k\beta)^{-1}$, with k the Boltzmann's constant, it is describable by a canonical ensemble with partition function

$$Z = \sum_\sigma e^{-\beta\mathcal{H}} \, . \tag{3}$$

The sum runs over all configurations of the set $\{\sigma_j\}$. The thermal average of σ_R is

$$\langle \sigma_R \rangle = Z^{-1} \sum_\sigma \sigma_R \, e^{-\beta\mathcal{H}} \, . \tag{4}$$

The Griffiths inequality which is useful in what follows is

$$\frac{\partial \langle \sigma_R \rangle}{\partial J(S)} \geq 0 \tag{5}$$

for all subsets R and S of Λ.

Now, consider two identical lattices labeled A and B, with interaction couplings $\{J_A(R)\}$ and $\{J_B(R)\}$, respectively. The corresponding entropies $S(J_A)$ and $S(J_B)$ satisfy the inequality[10]

$$S(J_B) - S(J_A) \geq k\beta \left(\langle \mathcal{H}_B \rangle_B - \langle \mathcal{H}_B \rangle_A\right). \tag{6}$$

The equality holds if and only if $(\mathcal{H}_B - \mathcal{H}_A)$ is a constant, independent of the set $\{\sigma_j\}$. $\langle X \rangle_A$ represents an average using the canonical distribution associated with system A. If it is assumed that

$$0 \leq J_B(R) \leq J_A(R) \tag{7}$$

for each set R in Λ, then we obtain

$$\langle \mathcal{H}_B \rangle_B - \langle \mathcal{H}_B \rangle_A = \sum_R J_B(R) \left(\langle \sigma_R \rangle_A - \langle \sigma_R \rangle_B\right) \geq 0 \tag{8}$$

because of (5) and (7). It follows from (6) that

$$S(J_A) \le S(J_B), \tag{9}$$

subject to (7). The inequality (9) means, simply, that an Ising ferromagnet's entropy decreases, and its order increases when one or more of its exchange couplings (or H) is increased.[11]

In order to make contact with TLT, consider first a one-dimensional Ising model with nearest-neighbor coupling $J>0$, and all other couplings identically equal to zero. For this system, the entropy $S_1(\beta, H, N)$ can be evaluated explicitly.[12] The thermodynamic entropy per particle $\sigma_1(\beta, H) = \lim_{N\to\infty} N^{-1} S_1$ exists and, in particular,

$$\lim_{\beta\to\infty} \sigma_1(\beta, H) = 0 \quad \text{for } H \ge 0. \tag{10}$$

The independence of the latter limit on H is a statement of TLT.

Envision now a "generalized" linear chain with the same H as above, with nearest-neighbor couplings $J_{ij}^{(nn)} \ge J > 0$, and with arbitrary other two-, three-, . . . , N-body ferromagnetic couplings such as in (2). Due to (9) and to the fact that the entropy is manifestly non-negative,[13] the generalized linear chain's entropy S_{1g} satisfies the relation

$$0 \le S_{1g}(\beta, H, N) \le S_1(\beta, H, N) \,. \tag{11}$$

If the couplings $\{J(R)\}$ are suitably chosen so that $\lim_{N\to\infty} N^{-1} S_{1g} = \sigma_{1g}(\beta, H)$ exists,[14] then the limit function $\sigma_{1g}(\beta, H)$ cannot exceed $\sigma_1(\beta, H)$ for a given β and H. This follows from (11), which holds for each member of the limiting sequence. As a consequence, we obtain

$$0 \le \lim_{\beta\to\infty} \sigma_{1g}(\beta, H) \le \lim_{\beta\to\infty} \sigma_1(\beta, H) = 0$$

for all $H \ge 0$, and σ_{1g} satisfies the TLT property [Eq. (10)].

An $M\times N$ two-dimensional Ising ferromagnet can be constructed using M identical generalized N-spin chains as the rows. When the rows are uncoupled, the system's entropy $S_2(\beta, H, NM)$ equals $MS_{1g}(\beta, H, N)$. In the thermodynamic limit, $M, N \to \infty$, we have $\sigma_2(\beta, H) = \sigma_{1g}(\beta, H)$, and the system obeys TLT. The addition of general ferromagnetic inter-row couplings in the $M\times N$ system lowers the entropy to $S_{2g}(\beta, H, NM)$, and (11) holds with N replaced by NM, and 1 by 2. Repeating the above arguments, it follows that a generalized two-dimensional system, for which $\sigma_{2g}(\beta, H)$ exists, satisfies the TLT property [Eq. (10)]. A three-dimensional generalized system can be constructed from many two-dimensional generalized systems by adding couplings between planes. In this way, an obvious extension of the above arguments shows that the three-dimensional generalized Ising ferromagnet satisfies TLT. A necessary condition in all of these proofs is the existence of the thermodynamic limit.[14] A sufficient condition is that all nearest-neighbor couplings be bounded from below by a positive constant. We further remark:

(i) The above proofs are built upon the result for a linear nearest-neighbor Ising ferromagnet with $J>0$. If J were taken to be zero, the third law would be violated for $H=0$.[12] (ii) Specific antiferromagnetic Ising models are known to violate TLT.[15] Thus, the mere inclusion of nonzero exchange couplings does not guarantee that TLT will be satisfied. (iii) The entropy monotonicity property displayed here provides upper bounds on σ for given unsolved models by comparing them with corresponding models with fewer bonds. For example, consider the following lattices, all with nearest-neighbor interactions only, and all with the same coupling constant J: face-centered cubic (fcc), simple cubic (sc), two-dimensional triangular (tr), simple square (ss), and linear (l). For a given β and H, the preceding entropy monotonicity arguments shows that $\sigma_{sc} \le \sigma_{ss} \le \sigma_1$. A bit of reflection shows that since the fcc lattice can be constructed by adding couplings between planar triangular lattices and since the latter in turn can be built from rows of one-dimensional chains, we obtain $\sigma_{fcc} \le \sigma_{tr} \le \sigma_1$. For $H=0$, both σ_{ss} and σ_{tr} are known.[16] Thus, one has upper bounds for σ_{sc} and σ_{fcc} for the zero-field case. For $H>0$, σ_1 provides an upper bound for σ_{ss}, σ_{tr}, σ_{sc}, and σ_{fcc}. (iv) It is easy to see that the average energy $\langle \mathcal{H} \rangle$ also satisfies a monotonicity property, because

$$\frac{\partial \langle \mathcal{H} \rangle}{\partial J(R')} = -\langle \sigma_{R'} \rangle - \sum_R J(R) \frac{\partial \langle \sigma_R \rangle}{\partial J(R')} \le 0.$$

The free energy $F = -\beta^{-1} \ln Z$ shares this property, since $\partial F / \partial J(R') = -\langle \sigma_{R'} \rangle \le 0$. It follows that both $\langle \mathcal{H} \rangle$ and F can be bounded from above for the cases discussed in (iii). (v) The present approach offers the possibility of proving TLT for quantum fluids. Since it is known that the ideal Bose and Fermi fluids satisfy TLT, such a proof rests upon the status of the inequality $S_{\text{nonideal}} \le S_{\text{ideal}}$ for specific classes of quantum fluids. Although this inequality holds for classical fluids and has been discussed for the quantum case,[10,17] a rigorous demonstration of its validity (or invalidity) is lacking. (vi) An elaboration of the points discussed here and a related discussion of magnetic cooling will be published elsewhere.[12]

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[11]J. Wilks, *The Third Law of Thermodynamics* (Oxford U. P., London, 1961).

[2]A systematic discussion of this point is contained in the Ph. D. thesis of S. J. Glass, Case Institute of Technology, 1958 (unpublished). Portions of this work are in the following publications: M. J. Klein and S. J. Glass, Phil. Mag. 3, 538 (1958); S. J. Glass and M. J. Klein, Physica 25, 277 (1959).

[3]An interesting, albeit nonrigorous, discussion of the third law, based upon the asymptotic behavior of the density of states, has been given by H. B. G. Casimir, Z. Physik 171, 246 (1963). Casimir's initial work on this problem (unpublished) preceded that of Glass (Ref. 2) and is discussed by Glass.

[4]Recently, it has been pointed out that classical systems which interact with electromagnetic radiation satisfy the third law. See T. H. Boyer, Phys. Rev. D 1, 1526 (1970).

[5]M. J. Klein, in *Termodinamica Dei Processi Irreversibili*, edited by S. R. DeGroot (N. Zanichelli, Bologna, 1960), p.1.

[6]R. B. Griffiths, J. Math. Phys. 8, 478 (1967); 8, 484 (1967).

[7]D. G. Kelly and S. Sherman, J. Math. Phys. 9, 466 (1968).

[8]See J. Ginibre, Phys. Rev. Letters 23, 828 (1969) and references therein.

[9]R. B. Griffiths, J. Math. Phys. 6, 1447 (1965).

[10]H. S. Leff, Am. J. Phys. 37, 548 (1969). This inequality is a direct consequence of the Gibbs-Bogoliubov inequality $F(\mathcal{H}_B) \leq F(\mathcal{H}_A) + \langle \mathcal{H}_B - \mathcal{H}_A \rangle_A$, where $F(\mathcal{H}_A) = \langle \quad _A \rangle_A - TS_A = -kT \ln Z_A$ (same expression holds with subscript B). A lengthy discussion of this and other related inequalities of Gibbs is given by H. Falk, Am. J. Phys. 38, 858 (1970).

[11]The inequality (9) can be obtained in other ways. (a) Using the expression $S = k \ln Z + k\beta \langle \mathcal{H} \rangle$, it follows from (2), (3), and (5) that $\partial S/\partial J(R') = -k\beta \sum_R J(R)\, \partial \langle \sigma_R \rangle / \partial J(R') \leq 0$. The derivatives are taken holding β and $\{J(R): R \neq R'\}$ fixed. (b) Recognizing that $S = -(\partial F/\partial T)_{J(R)}$ and $\langle \sigma_R \rangle = -[\partial F/\partial J(R)]_T$, the equality of the mixed second derivatives with respect to $J(R)$ and T, holding $\{J(R'): R' \neq R\}$ fixed, yields $[\partial S/\partial J(R)]_T = [\partial \langle \sigma_R \rangle / \partial T]_{J(R)}$. The right-hand side is nonpositive, since increasing T is equivalent to decreasing *all* of the $\{J(R)\}$ for fixed T.

[12]H. S. Leff (unpublished).

[13]The manifestly non-negative nature of S follows from the fact that $S = -k \sum_\sigma P(\sigma) \ln P(\sigma)$, where $0 \leq P(\sigma) = Z^{-1} \times e^{-\beta \mathcal{H}} \leq 1$.

[14]R. B. Griffiths, J. Math. Phys. 5, 1215 (1964).

[15]J. C. Bonner and M. E. Fisher, Proc. Phys. Soc. (London) 80, 508 (1962), and references therein.

[16]See, for example, M. E. Fisher, Rept. Progr. Phys. 30, 615 (1967), for a list of relevant references.

[17]R. Baierlein, Am. J. Phys. 36, 625 (1968).

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Restricted Lower Bounds in the Statistical Theory of Electronic Energies*

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The so-called quasiclassical approximations are shown to give, in a certain restricted sense, lower bounds to energy eigenvalues. Variational calculations of the energies of hydrogenlike atoms are carried out as an illustration.

I. INTRODUCTION

It is well known that the ground-state energies of neutral atoms calculated from the Thomas-Fermi theory[1,2] are lower than those observed. The original Thomas-Fermi density can be derived from a general formulation[3] of statistical theory by employing an independent-particle approximation and the assumption that the kinetic-energy and potential-energy operators of a particle commute. Such an assumption is illustrative of a set of so-called quasiclassical approximations. For these approximations, the Hamiltonian operator of the system is divided into two parts, the choice of which is a matter of convenience, and the two parts are assumed to commute with each other. In studying continuous bases of representation[4] for such approximations, the possible existence of a statistical analog of the Rayleigh-Ritz variational principle, that gives *lower bounds* to energy eigenvalues, was suggested. The purpose of this paper is to show that, formally, the quasiclassical approximations do give, in a certain restricted sense, such lower bounds to energy eigenvalues. Variational calculations of the energies of hydrogenlike atoms are carried out as an illustration of the use of this "principle of restricted lower bounds."

II. FORMAL THEORY

In terms of a general formulation of statistical theory, the density matrix associated with the M lowest-energy eigenstates of a many-electron system may be expressed as[3]

$$\rho_M(x_1, x_2) = \sum_{n=1}^{\infty} \Psi_n^*(x_1)\theta(\lambda_M - H)\Psi_n(x_2),$$

where the spectral operator $\theta(\lambda_M - H)$ is defined by