Journal of Statistical Physics, Vol. 24, No. 1, 1981

The Third Law of Thermodynamics and the Degeneracy of the Ground State for Lattice Systems

Michael Aizenman[1] and Elliott H. Lieb[1,2]

Received February 11, 1980

The third law of thermodynamics, in the sense that the entropy per unit volume goes to zero as the temperature goes to zero, is investigated within the framework of statistical mechanics for quantum and classical lattice models. We present two main results: (i) For all models the question of whether the third law is satisfied can be decided completely in terms of ground-state degeneracies alone, provided these are computed for all possible "boundary conditions." In principle, there is no need to investigate possible entropy contributions from low-lying excited states. (ii) The third law is shown to hold for ferromagnetic models by an analysis of the ground states.

KEY WORDS: Third law; entropy; thermodynamics; lattice systems; statistical mechanics.

1. INTRODUCTION

1.1. Questions Raised in the Past

The third law of thermodynamics, in Planck's form, is that the entropy density S for a bulk system at the temperature T approaches zero as $T \to 0$. The discussion of that rule from the vantage point of statistical mechanics has centered both on the question of its validity (it is known to have some notable exceptions, some of which we shall mention) and on its relation to the nondegeneracy of the system's Hamiltonian at its lowest, or ground state, energy.

Dedicated to Pierre Résibois. Work supported in part by NSF grant PHY-7825390 A01.

[1] Department of Physics, Princeton University, Princeton, New Jersey.
[2] Also at the Department of Mathematics, Princeton University, Princeton, New Jersey.

While the latter aspect of the third law is often put forward in textbooks, under closer scrutiny it was seriously questioned by Griffiths, among others (see Ref. 3). He pointed out[1,2] that:

1. For any finite system the entropy as $T \to 0$ is determined by the ground state degeneracy. However, for bulk systems it would be necessary to achieve a very low T in order to be sure that the system is effectively in its ground state. This T is usually unattainably small. In other words, what is effectively done in the laboratory corresponds to taking the thermodynamic limit first and then the limit $T \to 0$. Hence the interchange of the limits could lead to misleading conclusions about real situations.

2. There are lattice models which in finite volumes have nondegenerate ground states, but for which, nevertheless, the third law is not satisfied.

3. For (infinitely) large systems, the ground state contribution to the partition function is negligible at any nonzero temperature. Thus S_0, the limiting entropy density at $T = 0$, may depend crucially also on the distribution of low-energy excitations.

The discussion of the third law in Ref. 2 concludes with: "My good wishes to anyone who wants to embark on this quest, but let him remember that he must do *more* than examine the ground state!."

After the above warning, rigorous proofs of the third law for ferromagnetic lattice systems[4,5] avoided references to ground states and relied on less direct arguments, such as correlation inequalities or Lee–Yang techniques.

Our purpose in this paper is to show, for quantum and classical lattice systems, that the entropy density at $T = 0$ is indeed directly related to the degeneracy of the ground state when the latter is suitably interpreted. We will establish various forms of this relationship. These have value both conceptually and as a simpler tool for proving the third law for certain lattice systems (and computing the nonzero entropy for others).

We find it very useful to study the problem using the infinite system formalism. With regard to calculations of the zero-temperature entropy which are based on finite-volume ensembles, with the correct order of limits and some specified boundary conditions, we reach the following conclusions. For simplicity, these are stated for classical systems with finite-range interactions.

1. Griffiths is correct in asserting the need to take into account low-lying excitations. As he showed by an example (discussed here as Example 7) these can have bulk contribution to the entropy at $T = 0$. However, as we shall point out next, there is another way of finding all the contributions of these excitations.

2. If, for a sequence of finite regular domains, the number of excitations with energy of the order $o(V)$ grows exponentially with the volume V,

then, *necessarily*, for some proper boundary conditions the system has a highly degenerate ground state. The multitude of low-lying excitations can always be viewed as a result of the imposition of degeneracy-breaking boundary conditions. In the example referred to above, the degenerate ground states are clearly visible.

3. The contribution to the entropy, at $T = 0$, of the above-mentioned low-lying excitations is completely accounted for by counting the entropy of the ground states which correspond to boundary conditions with the highest degeneracy. Furthermore, there is no other subtle source of bulk entropy.

In Section 6 we use the relation which we have established between S_0 and the ground state degeneracy to give a simple proof of the third law for certain, classical and quantum, ferromagnetic models.

We have been recently informed that some of our results were also derived by Slawny.[14]

1.2. Definition of S_0

Entropy is conveniently viewed as a function of energy, since as such it is convex. The thermodynamic relation we shall use to define it in a finite volume Λ is

$$F_\Lambda = E - \beta^{-1} S_\Lambda(E) \tag{1.1}$$

where $\beta = 1/kT$ and the free energy of a system in the region Λ, $F_\Lambda = F_\Lambda(\beta)$, is obtained from its partition function $Z_\Lambda(\beta)$:

$$F_\Lambda(\beta) = -(1/\beta) P_\Lambda(\beta); \qquad P_\Lambda(\beta) = |\Lambda|^{-1} \ln Z_\Lambda(\beta) \tag{1.2}$$

with β such that

$$E = -(\partial/\partial\beta) P_\Lambda(\beta) \tag{1.3}$$

The existence of the thermodynamic limit for $F_\Lambda(\beta)$ is well understood, at least for a large class of lattice systems.[6] By a standard application of the convexity in β of $P_\Lambda(\beta)$, this implies that:

1. There is a thermodynamic limit e_0 for the ground state energy density and for the maximal energy density $e_{\max}$.

2. In the thermodynamic limit, $S_\Lambda(E)$ converges pointwise, in the interval $(e_0, e_{\max})$, to a function which we denote by $S(E)$.

3. The limit of $S_\Lambda(E)$ is independent of boundary conditions, for $E \in (e_0, e_{\max})$, and the function $S(\cdot)$ is convex (and, thus, continuous).

However, the above arguments do not yield convergence at the boundary point e_0. In fact, the limit of $S_\Lambda(e_0(\Lambda))$ may depend on the boundary conditions.

The main subject of our discussion is

$$S_0 = \lim_{E \downarrow e_0} S(E) \equiv \lim_{E \downarrow e_0} \lim_{\Lambda \uparrow \infty} S_\Lambda(E) \tag{1.4}$$

which *defines* the entropy density at $T = 0$ in the thermodynamic limit.

Thus we follow the canonical ensemble formalism, whose advantage is the convexity of $S_\Lambda(\cdot)$. With the physical restriction of $T \geqslant 0$, the above procedure does not define $S(E)$ on the full range of possible values of the energy density. This definition can be accomplished by considering all $\beta \in (-\infty, \infty)$. Alternatively, there is a variational characterization of $S(\cdot)$ on its full domain, to be mentioned in the next section, which avoids any reference to the temperature. Other definitions of $S(E)$ exist, corresponding to the various other ensembles, but they are known to agree with the above one in the thermodynamic limit.[1,6]

2. THE INFINITE-SYSTEM FORMULATION OF THE THERMODYNAMIC LIMIT

The analysis of the thermodynamic limit is facilitated by the infinite-system formalism,[6] which is very useful for this purpose. Our discussion will center on classical and quantum lattice systems.

With each lattice site $i \in \mathbf{L} = \mathbf{Z}^d$ (d is the dimension of the space) there is associated either a finite discrete space $\mathcal{H}_i^{(c)}$ or a finite-dimensional Hilbert space $\mathcal{H}_i^{(q)}$. For any finite $\Lambda \subset \mathbf{L}$ the observables measurable in Λ form an algebra $\mathcal{Q}_\Lambda$, which corresponds either to functions on $\Omega_\Lambda = \times_{i \in \Lambda} \mathcal{H}_i^{(c)}$ or operators (the *full* matrix algebra) on $\mathcal{H}_\Lambda = \times_{i \in \Lambda} \mathcal{H}_i^{(q)}$.

In both cases states of the system are represented by expectation value functionals (i.e., positive and normalized) ρ on the algebra of (quasilocal) observables $\mathcal{Q} = \overline{V \mathcal{Q}_\Lambda}$. In the case of classical systems, states correspond to probability measures on the "phase space" of the spin configurations of the infinite system, $\Omega = \times_{i \in \mathbf{L}} \mathcal{H}_i^{(c)}$.

For any $\Lambda \subset \mathbf{L}$, π_Λ will stand for the projection, or restriction, of the corresponding object to Λ. Thus $\pi_\Lambda \rho$ is either the probability distribution on Ω_Λ or, if applicable, the density operator on $\mathcal{H}_\Lambda$ which gives the restriction of ρ to $\mathcal{Q}_\Lambda$.

We denote the set of translation-invariant states by $\mathcal{I}$. The (information-theoretic) *entropy of a state* $\rho \in \mathcal{I}$ is defined via

$$s_\Lambda(\rho) = -|\Lambda|^{-1} \operatorname{tr}_\Lambda(\pi_\Lambda \rho) \ln(\pi_\Lambda \rho) \tag{2.1}$$

as the limit[7]

$$s(\rho) = \lim_{\Lambda \uparrow \mathbf{L}} s_\Lambda(\rho) \tag{2.2}$$

Here $\Lambda \uparrow \mathbf{L}$ means convergence over any sequence of finite domains in $\mathbf{L}$

which tend to L in the van Hove sense,[6] and the limit in (2.2) is independent of the sequence. In the classical case tr_Λ represents summation over Ω_Λ, which is a commonly used a-priori measure.

The Hamiltonian of the system is formally

$$H = \sum_{B \subset \mathrm{L}} \Phi_B \tag{2.3}$$

with $\Phi_B \in \mathcal{Q}_B$. We shall assume translation invariance of both $\{\mathcal{H}_i\}$ and $\{\Phi_B\}$. In that case the Hamiltonian density is given by

$$h = \sum_{B \ni 0} \frac{1}{|B|} \Phi_B \tag{2.4}$$

The partition function mentioned in (1.2) is

$$Z_\Lambda = \mathrm{tr}_\Lambda \exp\Bigl(-\sum_{B \in \Lambda} \Phi_B\Bigr) \tag{2.5}$$

and a sufficient condition for the convergence mentioned there, with

$$e_0 = \inf_{(\min)} \{\rho(h) \mid \rho \in \mathcal{S}\} \tag{2.6}$$

is that

$$\|\Phi\| \equiv \sum_{B \ni 0} \frac{1}{|B|} \|\Phi_B\| < \infty \tag{2.7}$$

$\|\Phi_B\|$ being the corresponding "sup" norm.

We will always assume $\|\Phi\| < \infty$.

The two entropy functions to which we have referred are related by the following variational principle:

$$S(E) = \sup\{s(\rho) \mid \rho \in \mathcal{S}, \rho(h) = E\} \tag{2.8}$$

for any $E \in (e_0, e_{\max})$.

Equation (2.8) follows from the variational principle for $P(\beta)$, found in Refs. 6 and 8, by the usual Legendre-transform technique, which is applicable because $P(\cdot)$ and $S(\cdot)$ are convex.

The supremum in (2.8) is always attainable. The translation-invariant states for which $s(\rho) = S(E)$, with $E = \rho(h)$, are all the equilibrium states, i.e., the translation-invariant Gibbs states,[6,8,9] or possibly [if $E(T)$ is discontinuous] convex combinations of such states.

3. A VARIATIONAL PRINCIPLE FOR S_0

At the end of the previous section we saw that the thermodynamic entropy density $S(E)$ is the entropy density $s(\rho)$ for certain (entropy-maximizing) states appropriate to the energy E. We shall now extend this result to S_0 [which corresponds to the boundary of the domain of definition of $S(\cdot)$]. We have $S_0 = s(\rho)$ for an appropriate, most degenerate, class of (ground) states.

Proposition 1. If $\|\Phi\| < \infty$, then

$$S_0 = \max\{s(\rho) \mid \rho \in \mathcal{I}, \quad \rho(h) = e_0\} \tag{3.1}$$

Proof. (i) Assume the existence of $\rho \in \mathcal{I}$ such that

$$\rho(h) = e_0, \qquad s(\rho) > S_0 \tag{3.2}$$

Let $\rho' \in \mathcal{I}$ be a state with $\rho'(h) > e_0$ and consider the states $\rho_\lambda = (1-\lambda)\rho + \lambda\rho'$, $\lambda \in [0,1]$. Both $\rho_\lambda(h)$ and $s(\rho_\lambda)$ are continuous (in fact affine[6]) functions of λ. {See Fig. 1, where the point A (resp. B) gives $s(\rho)$ [resp. $s(\rho')$] and the dotted line is $s(\rho_\lambda)$.} Since $S(\cdot)$ is continuous, (3.2) implies that for small enough $\lambda \in (0, 1]$

$$s(\rho_\lambda) > s(\rho_\lambda(h)) \tag{3.3}$$

That would contradict (2.6). Thus

$$S_0 \geqslant \sup\{s(\rho) \mid \rho \in \mathcal{I}, \quad \rho(h) = e_0\} \tag{3.4}$$

(ii) To conclude the proof, choose a weakly convergent sequence $\rho_n \xrightarrow{w} \bar{\rho}$ for which

$$\rho_n(h) \to e_0, \qquad s(\rho_n) \geqslant S(\rho_n(h)) - 2^{-n} \tag{3.5}$$

The existence of such a sequence follows from (2.8). Since $s(\rho)$ is an upper semicontinuous function on $\mathcal{I}$,[6,7] we get

$$s(\bar{\rho}) \geqslant \lim_{n\to\infty} \sup s(\rho_n) \geqslant \lim_{n\to\infty} S(\rho_n(h)) = S_0 \tag{3.6}$$

while

$$\bar{\rho}(h) = \lim_{n\to\infty} \rho_n(h) = e_0$$

Combining (3.4) with (3.6), we see that the supremum in (3.4) is attained and that (3.1) holds. $\square$

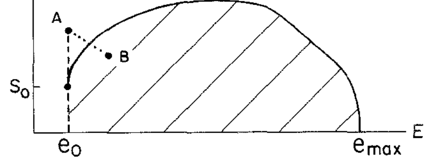

Fig. 1. The general form of $S(E)$. If $S_0 \neq 0$, then the system may have various translation-invariant, energy-minimizing states with different entropies (see Section 4). The dotted line is to illustrate an argument made in the proof of Proposition 1. The shaded area is the range of possible values of $(\rho(h), s(\rho))$ for $\rho \in \mathcal{I}$.

Corollary 1. If $\rho \in \mathcal{G}$ is a weak limit of Gibbs states $\rho_n \in \mathcal{G}$ at temperatures T_n, with $T_n \to 0$, then

$$s(\rho) = S_0 \tag{3.7}$$

Proof. For Gibbs states $s(\rho_n) = S(\rho_n(h))$. Furthermore, $T_n \to 0$ implies that $\rho_n(h) \to e_0$. Thus the arguments in the second part of the above proof apply to ρ_n, and prove (3.7). □

Remark. Corollary 1 provides us with a method of computing S_0. For example, it is known (e.g., by Peierls' argument) that the $T = 0$ limit of the "+ states" of the Ising model in $d \geqslant 2$, with $h \geqslant 0$, is concentrated on the single configuration: $\sigma_i = +1$, $\forall i \in \mathsf{L}$. Thus for this model $S_0 = 0$. The Peierls argument was mentioned merely to illustrate the use of Corollary 1. A better proof of the third law for ferromagnets will proceed directly from Theorem I and will be given in Section 6.

4. S_0 AND THE DEGENERACY OF GROUND STATES FOR CLASSICAL LATTICE SYSTEMS

Proposition 1 provides a characterization of S_0 as the maximal entropy density of a translation-invariant ground state. For classical systems we can also relate it to the number of ground state configurations. Let us first clarify this concept.

Definition 1. Let Φ be an interaction of a classical system with $\sum_{B \ni 0} \|\Phi_B\| < \infty$. A spin configuration $\sigma \in \Omega$ is a *ground state configuration for* $\Lambda \subset \mathsf{L}$ if for any $\sigma' \in \Omega$ that differs from σ only in Λ, i.e., $\sigma_{\Lambda^c} = \sigma'_{\Lambda^c}$,

$$\sum_{\substack{B \subset \mathsf{L} \\ B \cap \Lambda \neq 0}} \left[\Phi_B(\sigma') - \Phi_B(\sigma)\right] \geqslant 0 \tag{4.1}$$

We denote the collection of such configurations by G_Λ and call the elements of

$$G = \bigcap_{\substack{\Lambda \subset \mathsf{L} \\ |\Lambda| < \infty}} G_\Lambda$$

ground state configurations.

The local energy minimization condition (4.1) gives rise to the set $\pi_\Lambda G_\Lambda \in \Omega_\Lambda$. Notice that while

$$\pi_\Lambda G \subset \pi_\Lambda G_\Lambda \tag{4.2}$$

equality in (4.2) is not generally true. There may be configurations in Λ which for certain boundary conditions (i.e., extensions to the whole of L) minimize the energy with respect to variations in Λ, but which nevertheless cannot be completed to ground state configurations on the whole lattice L.

Example 1. An example of the above situation is provided by the nearest neighbor, ferromagnetic Ising spin configuration in a $4L \times L$ box ($d = 2$), for which $\sigma \equiv -1$ on a $2L \times L$ column, symmetrically placed between two $L \times L$ columns on which $\sigma \equiv +1$. This configuration can be extended to L by making the $2L \times L$ column into a $2L \times \infty$ column of minus spins, all the others being plus. This extended configuration cannot be changed inside Λ without raising the energy. However, there is no extension with the property that the energy cannot be lowered by changing the spins in some finite box.

It should not be assumed that the presence of both negative and positive spins in σ is the reason that σ is not a ground state configuration. The configurations in which $\sigma_i = -1$ if $i_x \leqslant x_0$ $[i = (i_x, i_y)]$ and $\sigma_i = +1$ if $i_x > x_0$ are in G.

Example 2. For an interaction of finite range one can ask whether all the ground states can be characterized by a local condition, i.e., whether G is identical with the set

$$\{\sigma \in \Omega \,|\, \pi_\Lambda \sigma \in \pi_\Lambda G, \quad \forall \Lambda \subset \mathsf{L} \quad \text{with diam} \quad \Lambda < R\}$$

for some $R < \infty$. That is not the case. For example, for the nearest neighbor ferromagnetic Ising system ($d = 2$), and any R, the configuration

$$\sigma = \begin{cases} +1 & |x|, |y| \leqslant R/2 \\ -1 & \text{otherwise} \end{cases}$$

is in the above set, but not in G.

Definition 2. The quantities

$$D_\Lambda = \ln \operatorname{card}(\pi_\Lambda G), \qquad D_\Lambda^* = \ln \operatorname{card}(\pi_\Lambda G_\Lambda)$$

where card (A) is number of elements in a set A, are called *ground state configurational entropies in the domain* Λ.

The quantities D_Λ and D_Λ^* have some properties similar to those of entropy of states. It is easy to see that D_Λ and D_Λ^* are subadditive, i.e., if $\Lambda = \Lambda_1 \cup \Lambda_2$ with Λ_1, Λ_2 disjoint, then

$$D^{(*)}_\Lambda \leqslant D^{(*)}_{\Lambda_1} + D^{(*)}_{\Lambda_2} \tag{4.3}$$

Furthermore, by (4.2)

$$D_\Lambda \leqslant D_\Lambda^* \tag{4.4}$$

Remark. Entropy is not only subadditive but also strongly subadditive, i.e.,

$$S_{\Lambda_1 \cup \Lambda_2 \cup \Lambda_3} + S_{\Lambda_3} \leqslant S_{\Lambda_1 \cup \Lambda_3} + S_{\Lambda_2 \cup \Lambda_3} \tag{4.5}$$

for three disjoint domains. We do not know under which conditions (4.5) holds for D^*_Λ.

By standard arguments,[6] (4.5) implies the following result:

Proposition 2. The following two limits exist:

$$d^{(*)} = \lim_{\Lambda \uparrow \mathbf{L}} |\Lambda|^{-1} D^{(*)}_\Lambda \tag{4.6}$$

for any sequence of rectangles increasing to $\mathbf{L}$, or for any regular sequence in the sense of Ref. 10. The limit is independent of the sequence.

Now we come to the main facts about $D^{(*)}_\Lambda$ and S_0.

Proposition 3.

$$d = d^* = S_0 \tag{4.7}$$

Proof. In view of (4.4), it is enough to show that

$$d \geqslant S_0 \geqslant d^* \tag{4.8}$$

(i) Let $\rho \in \mathcal{I}$, $\rho(h) = e_0$. We claim this implies that

$$\rho(G) = 1 \tag{4.9}$$

(Here ρ is being thought of as a probability measure on the set of configurations.) For any finite cubic region Λ there is a transformation $T_\Lambda : \Omega \to G_\Lambda$ which modifies any configuration σ only in Λ, mapping it on one which minimizes the energy subject to the boundary conditions σ_Λ. If $\rho(G) < 1$, then for some Λ this map lowers the energy with positive probability, i.e.,

$$\rho\Big(\sum_{B \cap \Lambda \neq \varnothing} \big[\Phi_B(T_\Lambda \cdot) - \Phi_B(\cdot) \big] \Big) = -\Delta E < 0 \tag{4.10}$$

Now choose k large enough so that

$$\epsilon(k) \equiv \sum_{\substack{B \ni 0 \\ \operatorname{diam} B \geqslant k}} \|\Phi_B\| < \frac{\Delta E}{10|\Lambda|} \tag{4.11}$$

and let $\{\Lambda_n\}_{n=1,2,\dots}$ be the collection, ordered in some way, of the translates of Λ by vectors in the sublattice $(k + \operatorname{diam}\Lambda)\mathbf{L}$. In order to produce a state with a lower energy density than ρ, we construct

$$\rho_n(\cdot) = T_{\Lambda_n} \cdot T_{\Lambda_{n-1}} \cdots T_{\Lambda_1} \rho(\cdot)$$

While the energy decreases produced by subsequent applications of T_{Λ_n} may be smaller than ΔE, we still have (since $\{\Lambda_n\}$ are at least the distance k apart)

$$\begin{aligned}&\rho_n\Big(\sum_{B\cap\Lambda_n\neq\varnothing}\Phi_B(\cdot)\Big)-\rho_{n-1}\Big(\sum_{B\cap\Lambda_n\neq\varnothing}\Phi_B(\cdot)\Big)\\&\quad\leqslant\rho\Big(\sum_{B\cap\Lambda_n\neq\varnothing}\big[\Phi_B(T_{\Lambda_n}\cdot)-\Phi_B(\cdot)\big]\Big)+\epsilon(k)|\Lambda|\leqslant-\tfrac{4}{5}\Delta E\end{aligned}\tag{4.12}$$

Thus the total gain in energy is proportional to n:

$$\begin{aligned}&\rho_n\Big(\sum_{B\cap(\cup_1^n\Lambda_m)\neq\varnothing}\Phi_B(\cdot)\Big)-\rho\Big(\sum_{B\cap(\cup_1^n\Lambda_m)\neq\varnothing}\Phi_B(\cdot)\Big)\\&\quad=\sum_{m=1}^{n}\rho_n\Big(\sum_{B\cap\Lambda_n\neq\varnothing}\Phi_B(\cdot)\Big)-\rho_{n-1}\Big(\sum_{B\cap\Lambda_n\neq\varnothing}\Phi_B(\cdot)\Big)\leqslant-\tfrac{4}{5}\Delta E\cdot n\end{aligned}\tag{4.13}$$

In the limit $n\to\infty$ the states ρ_n converge locally (i.e., weakly) to some state ρ_∞. Averaging ρ_∞ over translations, we obtain a state $\bar\rho\in\mathfrak{T}$, for which [using (4.13)]

$$\bar\rho(h)\leqslant e_0-(k+\operatorname{diam}\Lambda)^{-d}\tfrac{4}{5}\,\Delta E<e_0\tag{4.14}$$

(4.14) is a contradiction, which proves (4.9).

The measure $\pi_\Lambda\rho$ is thus concentrated on $\pi_\Lambda G$. By a well-known upper bound on the entropy of a probability distribution over a finite set of N points, $S\leqslant\ln N$, this implies that

$$s_\Lambda(\rho)\leqslant(1/|\Lambda|)D_\Lambda\tag{4.15}$$

(4.15), combined with Proposition 1, proves the first inequality in (4.8).

(ii) We shall prove the second inequality by a variational argument. First, notice the following bound on the interaction across the boundary of any domain $\Lambda\subset\mathsf{L}$:

$$\sum_{\substack{B\cap\Lambda\neq\varnothing\\B\cap\Lambda^c\neq\varnothing}}\|\Phi_B\|=\sum_{X\in\Lambda}\frac{1}{B\cap\Lambda}\|\Phi_B\|\leqslant|\Lambda|b_\Lambda\tag{4.16}$$

with

$$f_\Lambda(k)=|\{x\in\Lambda\,|\,\operatorname{dist}(x,\Lambda^c)=k\}|/|\Lambda|$$

$$b_\Lambda=\sum_{k=0}^{\infty}f_\Lambda(k)\epsilon(k)$$

and the $\epsilon(k)$ defined in (4.11).

Equation (4.16) implies for any ground state configuration in Λ, $\sigma\in G_\Lambda$, that for all $\hat\sigma\in\Omega$

$$\frac{1}{|\Lambda|}\sum_{B\subset\Lambda}\Phi_B(\sigma)\leqslant\frac{1}{|\Lambda|}\sum_{B\subset\Lambda}\Phi_B(\hat\sigma)+2b_\Lambda\tag{4.17}$$

With σ fixed, take expectation values of both sides of (4.17) in any translation-invariant ground state $\hat{\rho}$ for $\hat{\sigma}$. Using (4.16) once again, we find that for any $\sigma \in G_\Lambda$

$$\frac{1}{|\Lambda|}\sum_{B\subset\Lambda}\Phi_B(\sigma) \leqslant e_0 - \hat{\rho}\left[\sum_{\substack{B\cap\Lambda\neq\varnothing\\ B\cap\Lambda^c\neq\varnothing}}\frac{|B\cap\Lambda|}{|B|}\Phi_B(\hat{\sigma})\right] + 2b_\Lambda \leqslant e_0 + 3b_\Lambda \tag{4.18}$$

Consider now a rectangular partition of L, Λ being the basic cube, and let $\rho^{(\Lambda)}$ be the (product) state for which the spins in each cube are equally distributed (with equal weights) on all the configurations in $\pi_\Lambda G_\Lambda$, independently of the spins in the other cubes. If $\hat{\rho}^{(\Lambda)} \in \mathcal{G}$ is the state obtained from $\rho^{(\Lambda)}$ by averaging over the translations then, since $\hat{\rho}^{(\Lambda)}$ and $\rho^{(\Lambda)}$ have the same entropies for a corresponding subgroup of translations (by the argument in Ref. 6, Proposition 7.2.3),

$$s(\hat{\rho}^{(\Lambda)}) = (1/|\Lambda|)D_\Lambda^* \tag{4.19}$$

and, using (4.18) and (4.16),

$$\hat{\rho}^{(\Lambda)}(h) \leqslant e_0 + 4b_\Lambda \tag{4.20}$$

By the variational principle for $S(\cdot)$, (2.8) and (3.1), this implies

$$\sup\{S(e)\,|\,e\in[e_0, e_0+4b_\Lambda]\} \geqslant \frac{1}{|\Lambda|} \quad \ln\operatorname{card}(\pi_\Lambda G_\Lambda) \tag{4.21}$$

Letting $\Lambda\uparrow$L (along a sequence of cubes), we have

$$\lim_{\Lambda\uparrow\mathsf{L}} b_\Lambda = \lim_{\Lambda\uparrow\mathsf{L}}\sum_{k=0}^{\infty} f_\Lambda(k)\epsilon(k) = 0 \tag{4.22}$$

since $f_\Lambda(k)\to 0$ for any k and $\epsilon(k)\to 0$ as $k\to\infty$, while $\sum_{k=0}^{\infty} f_\Lambda(k) = 1$. This leads to the conclusion that $S_0 \geqslant d^*$. $\square$

In step (i) of the above proof it was shown that $\rho(G) = 1$ for any state ρ such that (1) $\rho\in\mathcal{G}$ and (2) $\rho(h) = e_0$. In many situations (see Examples 3 and 4) there is a smaller set of ground state configurations $\hat{G}\subset G$ which supports the translation-invariant ground states, i.e., such that $\rho(\hat{G}) = 1$ for any ρ with the above properties 1 and 2. We shall generically denote such a set by $\hat{G}$, although we have not defined it uniquely for the general case. A very useful (see Section 6) strengthening of Proposition 2 is its following corollary, which holds for any version of a set $\hat{G}$ with the above property.

Corollary 2.

$$\lim_{\Lambda\uparrow\mathsf{L}}\frac{1}{|\Lambda|} \quad \ln\operatorname{card}\pi_\Lambda\hat{G} = S_0 \tag{4.23}$$

for any regular sequence of domains.

Proof. The conclusion of step (i) of the proof of Proposition 2 [which implies (4.22) for G rather than $\hat{G}$] holds for $\hat{G}$ by its defining characterization. The only other property of G on which the proof relied is (4.2), and it is also satisfied by $\hat{G}$. □

Example 3. For the two-dimensional Ising model (with $h = -\sum_{|i|=1} \frac{1}{2} \sigma_0 \sigma_i$), $e_0 = -2$. Thus $\rho \in \mathcal{G}$, $\rho(h) = e_0$ implies that $\sigma_i \sigma_j = +1$ with ρ probability 1, for any $i, j \in \mathbf{Z}^2$, $|i - j| = 1$. It follows that one may choose $\hat{G}$ to consist of the two configurations $\sigma_i \equiv +1$ and $\sigma_i \equiv -1$. On the other hand, G for this system is an infinite set, as we saw at the end of the discussion of Example 2.

As we shall see now, for finite-range interactions we can restrict $\hat{G}$ by a rigidness condition, whenever $S_0 = 0$.

Definition 3. A ground state configuration $\sigma \in G$ is *rigid* if, for any finite $\Lambda \subset \mathsf{L}, \sigma_\Lambda$ is the unique energy-minimizing configuration with the boundary condition σ_{Λ^c}.

Example 4. The Ising model, $d = 2$, configuration, for which $\sigma_i = +1$ if $i_x, i_y \geqslant 0$ and $\sigma_i = -1$ otherwise, is a ground state configuration which is not rigid. The same is true for any configuration with a single contour which has a step (whose position cannot be fixed by a boundary condition). However, the configuration mentioned at the end of Example 2, with a single straight contour line, is rigid.

Proposition 4. If $S_0 = 0$ for a system with finite-range interaction, then any translation-invariant ground state, i.e., $\rho \in \mathcal{G}$ with $\rho(h) = e$, is supported on the set of rigid configurations in G.

Proof. Let ρ be a state for which the above assumptions are satisfied, Λ a finite domain in L, and R the interaction range. Viewing ρ as a measure on the space of the configurations σ, let ϵ be the probability that the boundary condition σ_{Λ^c} does not have a unique ground state in Λ. We shall now show that

$$S_0 \geqslant \epsilon (R + \operatorname{diam} \Lambda)^{-d} \tfrac{1}{2} \ln 2 \tag{4.24}$$

(4.2) would clearly imply the stated conclusion.

Consider the collection $\{\Lambda_n\}$ of translates of Λ by vectors in the sublattice $(R + \operatorname{diam} \Lambda)\mathsf{L}$. Let $g_k(\sigma)$ be the function which for each configuration gives the fraction of boxes, among $\{\Lambda_1, \ldots, \Lambda_k\}$, in which $\sigma_{\Lambda_i^c}$ does not have a unique ground state. By the translation invariance of ρ, the expectation value of $g_k(\sigma)$ is ϵ. Since $0 \leqslant g_k(\cdot) \leqslant 1$

$$\epsilon = \rho(g_k(\cdot)) \leqslant \epsilon/2 + \rho(\{\sigma \in \Omega \mid g_k(\sigma) \geqslant \epsilon/2\}) \tag{4.25}$$

and we see that

$$\rho(\{\sigma \in \Omega \mid g_k(\sigma) \geqslant \epsilon/2\}) \geqslant \epsilon/2 \tag{4.26}$$

We now define ρ' as the state obtained from ρ by redistributing σ in $\bigcup_1^\infty \Lambda_n$, for any given values of σ in

$$A = \left(\bigcup_1^\infty \Lambda_n \right)^c,$$

equally among all the ground states in that set. Since the $\{\Lambda_n\}$ are at least a distance R apart, this conditional distribution has the product structure. It follows therefore, using (4.26), that the entropy density of ρ' with respect to the sublattice $(R + \operatorname{diam} \Lambda)\mathrm{L}$, is at least $(R + \operatorname{diam} \Lambda)^{-d}\epsilon/2 \ln 2$. By averaging ρ' over translations we obtain a translation-invariant ground state $\bar{\rho}$ with the same entropy (by a standard argument to which we referred in the proof of Proposition 2).

Now (4.24) follows by the variational principle of Proposition 1, applied to $\bar{\rho}$. □

For systems with finite-range interactions we also have:

Corollary 3. Let $N_\Lambda(b_\Lambda)$ denote the degeneracy of the ground state in Λ with the boundary condition $b_\Lambda \in \Omega_{\Lambda^c}$. If Φ is an interaction of finite range, the following limit exists and

$$\lim_{\Lambda \uparrow \infty} \sup_{b_\Lambda \in \Omega_{\Lambda^c}} \frac{1}{|\Lambda|} \ln N_\Lambda(b_\Lambda) = S_0 \tag{4.27}$$

Proof. Let the interaction range be R. The number of inequivalent boundary conditions for Λ is bounded by $\exp(\alpha C_d R |\partial\Lambda|)$, where $\exp(\alpha)$ is the number of points in $\mathcal{K}_0^{(c)}$ and C_d is a dimension-dependent constant. Therefore

$$N_\Lambda(b_\Lambda) \leqslant \operatorname{card} \pi_\Lambda G_\Lambda \leqslant N_\Lambda(b_\Lambda) \exp(\alpha C_d R |\partial\Lambda|) \tag{4.28}$$

Substituting (4.28) in (4.3), we get (4.27). □

Thus we have found an answer to Griffith's puzzle. While the third law is not implied by the nondegeneracy of the finite-volume systems with certain boundary conditions, S_0 still counts the maximal degeneracy. What for a given boundary condition may seem as a bulk contribution to the entropy due to low-lying excitations, may also be accounted for as a boundary effect!

Systems for which $S_0 \neq 0$ may, nevertheless, have ground states with zero entropy which satisfy the $T = 0$ version of the Dobrushin–Lanford–Ruelle equilibrium condition.[8] An example is the $d = 2$ antiferromagnetic triangular lattice Ising model discussed in Ref. 9, in which it is possible to suppress the ground state degeneracy by fixing the spins in one row to be all $+$. By Proposition 1 such states cannot be attained as limits of equilibrium states with $T \to 0$. We can now see the reason for it. $S_0 \neq 0$ implies that the system has more degenerate boundary conditions. If at any fixed $T \neq 0$ one tries to impose the nondegenerate boundary, as soon as Λ is large enough free energy considerations favor spontaneous change of the spins in a boundary layer.

5. QUANTUM LATTICE SYSTEMS

We shall now introduce the notion of ground states for infinite quantum lattice systems. This will enable us to extend to such systems the basic relation between S_0 and the degeneracy in finite volume. However, there will not be a simple analog of Corollary 3.

A basic property of ground states, and of the ground state configurations discussed in Section 4, is the minimization of the energy with respect to local perturbations. The formalization of the notion of local perturbation of a quantum system leads to an interesting observation. A natural definition, which draws on the properties of the mapping induced on $\mathscr{A}$ by the mapping $T_\Lambda : \Omega \to \Omega$ discussed in Section 4, is:

Definition 4. Let $\mathscr{A}$ be the algebra of observables of an infinite quantum lattice system. A local perturbation in $\Lambda \subset \mathsf{L}$ is a linear mapping T: $\mathscr{A} \to \mathscr{A}$ such that:

(a) $T(A) \geqslant 0$ for any $A \geqslant 0$.

(b) $T(A) = A$ for any $A \in \mathscr{A}_{\Lambda^c}$ [in particular $T(1) = 1$].

(In our shorthand notation $A = 1_\Lambda \otimes A \in \mathscr{A}$, for $A \in \mathscr{A}_{\Lambda^c}$.)

It turns out[12] that quite generally the above properties imply also:

(c) $T(X) \in \mathscr{A}_\Lambda$ for any $X \in \mathscr{A}_\Lambda$.

(d) $T(XY) = T(X)Y$ for any $X \in \mathscr{A}_\Lambda$, $Y \in \mathscr{A}_{\Lambda^c}$.

(e) T is completely positive.

It is gratifying to have (e), which is sometimes imposed on physical grounds.[13] However, it may seem surprising that (c) is true, because it is not implied in the classical case. In Section 4 we used local perturbations, which also satisfy (a) and (b), for which the change produced in Λ could also depend on the configuration in Λ^c (without modifying it). As we see, there are no such perturbations, in the sense of action on the observables in a state-independent way, for quantum systems. In view of the fact that a classical system (e.g., Ising model) can be thought of as a special quantum system, it may seem that there is a paradox here. There is none. The reason that (c) is true quantum mechanically is that we insisted upon $\mathscr{A}_\Lambda$ being the full matrix algebra. Noncommutativity plays a role in (c).

If it is desired to have consistency between the quantum and classical definitions of local perturbations and of the ground states (to be defined shortly), one could follow either of the following paths:

1. Impose (c) as a restriction in the definition of local perturbations in Section 4.

2. Define local perturbations directly on states. Or, equivalently, use a state-dependent definition, replacing (b) by

(b′) $\rho(T(A)) = \rho(A)$ for any $A \in \mathcal{Q}_{\Lambda^c}$.

We shall not bother to do either. Let us, however, remark that, had we followed path 1, the set of classical ground states G would not have been changed, although G_Λ would have been.

Definition 5. Let Φ be an interaction of a quantum system with $\sum_{B \ni 0} \|\Phi_B\| < \infty$. A state ρ is a ground state in Λ if for any local perturbation T in Λ

$$\sum_{B \cap \Lambda \neq \emptyset} \left[\rho(T\Phi_B) - \rho(\Phi)\right] \geqslant 0 \tag{5.1}$$

We denote the collection of ground states in Λ by $\mathcal{G}_\Lambda$, and call the elements of

$$\mathcal{G} = \bigcap_{\substack{\Lambda \subset \mathbf{L} \\ |\Lambda| < \infty}} \mathcal{G}_\Lambda$$

the ground states of the systems.

For quantum systems we define Q and Q^*, in analogy to $D^{(*)}$, by

$$Q^{(*)} = \sup\{s_\Lambda(\rho) \mid \rho \in \mathcal{G}_{(\Lambda)}\} \tag{5.2}$$

For classical systems, when viewed as quantum, Q and D are the same (but Q^* and D^* are not).

With the corresponding substitutions, the proof of Proposition 2 carries through, almost verbatim, to the quantum case. In particular, (4.3) corresponds to a well-known subadditivity of entropy. Thus we have:

Proposition 5. The following limits, through sequences of regular domains, exist and

$$\lim_{\Lambda \uparrow \mathbf{L}} \frac{1}{|\Lambda|} Q_\Lambda = \lim_{\Lambda \uparrow \mathbf{L}} \frac{1}{|\Lambda|} Q^*_\Lambda = S_0 \tag{5.3}$$

6. APPLICATIONS OF THE THEORY TO SPECIFIC MODELS

6.1. The Third Law for Ferromagnetic Models

We shall now demonstrate how to use the relation of S_0 to the ground state degeneracy, or entropy, to prove the third law for certain systems. A common simplifying feature in Examples 5 and 6 is that all the terms of the interaction $\{\Phi_B\}$ can attain their minima simultaneously. Consequently, e_0 can be computed, and $\mathcal{G}$ consists of states which minimize each Φ_B. This does not apply to the third example (and to that referred to in Ref. 9), where nevertheless one may still find e_0 by grouping $\{\Phi_B\}$ into larger units.

Example 5. Ferromagnetic Ising systems. These are classical systems with the spin variables σ_i having values in $\mathcal{K}_i = \{-\mathrm{L}, -\mathrm{L}+1, \ldots, \mathrm{L}\}$ and the Hamiltonian

$$H = -\sum J_B \sigma_B \tag{6.1}$$

where $\sigma_B = \prod_{i \in B} \sigma_i$ and

$$J_B \geqslant 0 \qquad \forall B \subset \mathrm{L} \tag{6.2}$$

Proposition 6. $S_0 = 0$ for any ferromagnetic Ising system with $H \neq 0$.

Proof. The interactions $\Phi_B = J_B \sigma_B$ attain their minima on the configuration $\sigma \equiv +1$ (among others, possibly). Thus $e_0 = \sum_{B \ni 0}(1/|B|)J_B$, and $\rho(h) = e_0$ if and only if

$$\rho(\sigma_B) = \mathrm{L}^{|B|} \tag{6.3}$$

for any $B \subset \mathrm{L}$ such that $J_B \neq 0$.

Since $\mathrm{L}^{|B|}$ is the maximal value that σ_B takes, (6.3) implies that $\hat{G}$, the support of the translation-invariant, energy-minimizing states (cf. Section 4), consists of configurations for which

$$\sigma_B = 1 \tag{6.4}$$

whenever $J_B \neq 0$.

We now claim that for any cube Λ

$$\operatorname{card} \pi_\Lambda \hat{G} \leqslant 2^{C|\partial\Lambda|} \tag{6.5}$$

with some fixed $C = C(J) < \infty$. To see this choose $B_0 \subset \mathrm{L}$ such that $J_{B_0} \neq 0$. Then (6.5) follows from the observation that, using (6.4) over all the translates of B_0, the values of σ in Λ, for $\sigma \in \hat{G}$, can be uniquely reconstructed from the values in the shell of width $\operatorname{diam} B_0$ surrounding Λ.

(6.5) implies that for any ρ as above

$$s_\Lambda(\rho) \leqslant C(|\partial\Lambda|/|\Lambda|)\ln 2 \to 0 \tag{6.6}$$

as $\Lambda \uparrow \mathrm{L}$. By Proposition 1 this proves that $S_0 = 0$. □

The above result is not new, having been proven in Refs. 4 and 5. However, as we have already mentioned, the previous proofs relied on less direct arguments, such as correlation inequalities or Lee–Yang methods.

Example 6. Quantum Heisenberg ferromagnet. The system consists of the usual quantum spin-1/2 variables $\boldsymbol{\sigma}_i = (\sigma_i^{(x)}, \sigma_i^{(y)}, \sigma_i^{(z)})$, interacting via

$$H = -\sum J_{ij}\boldsymbol{\sigma}_i \cdot \boldsymbol{\sigma}_j \tag{6.7}$$

with translation-invariant $J_{ij} \geqslant 0$. In the most common model J couples nearest neighboring spins, but we shall not make this assumption.

Proposition 7. $S_0 = 0$ for any ferromagnetic Heisenberg model with nonzero interaction.

Proof. By well-known properties of spins,

$$\boldsymbol{\sigma}_i \cdot \boldsymbol{\sigma}_j = \tfrac{1}{2}(\boldsymbol{\sigma}_i + \boldsymbol{\sigma}_j)^2 - \tfrac{1}{2}\left(\boldsymbol{\sigma}_i^2 + \boldsymbol{\sigma}_j^2\right) = P_{ij} - \tfrac{3}{4} \tag{6.8}$$

where P_{ij} is the projection on the symmetric subspace for the (i, j) permutation. Thus, while the $\{\Phi_B\}$ do not commute, any finite number of them can attain their minima simultaneously (on the corresponding totally symmetric, or maximal angular momentum space). Therefore we can compute e_0 and, what is more important, conclude that $\rho \in \mathcal{G}$ and $\rho(h) = e_0$ imply

$$\rho(\boldsymbol{\sigma}_i \cdot \boldsymbol{\sigma}_j) = \tfrac{1}{4}, \qquad \rho(P_{ij}) = 1 \tag{6.9}$$

for each (i, j) with $J_{ij} \neq 0$.

For the sake of clarity, we shall first consider the usual nearest neighbor model. Generally $\rho(P_{ij}) = \rho(P_{jk}) = 1$ implies $\rho(P_{ik}) = 1$. Thus the transitivity of J and (6.9) imply that for any ρ that satisfies the above conditions, (6.9) holds for any (i, j). Consequently, for any $\Lambda \subset \mathsf{L}$, $\pi_\Lambda \rho$ is concentrated on the $(|\Lambda| + 1)$-dimensional (Hilbert space) subspace of completely symmetric functions, corresponding to

$$\left(\sum_{i \in \mathfrak{L}} \boldsymbol{\sigma}_i\right)^2 = \tfrac{1}{2}|\Lambda|\left(\tfrac{1}{2}|\Lambda| + 1\right)$$

By a well-known upper bound on the entropy of a density operator of finite rank, this leads to

$$s(\rho)_\Lambda \leqslant (1/|\Lambda|)\ln(|\Lambda| + 1) \tag{6.10}$$

Invoking Proposition 1, we conclude that $S_0 = 0$.

To conclude the proof, we note that in the general case any Λ is decomposed into a finite number of connected components, by J_{ij}. As in Example 1, this number is bounded by const $\cdot\, (\operatorname{diam} B_0) \cdot |\partial\Lambda|$. In each component the total angular momentum must be maximal. Therefore $s_\Lambda(\rho)$ is bounded by the sum of the right sides of (6.6) and (6.10). Again, $S_0 = 0$. $\square$

The above argument does not apply to antiferromagnets, since there the $\{\Phi_B\}$ do not attain their minima simultaneously. The proof that $S_0 = 0$ for such systems is a very intriguing *open problem*.

6.2. Examples of Systems Which Violate the Third Law

Example 7. The following system, with $S_0 \neq 0$, has been considered by Griffiths,[1,2] who used it to demonstrate the need to consider low-lying excitations. The system, in $d = 3$, consists of spin variables which take the values $\sigma_i = 0, \pm 1$, and interact via the Hamiltonian

$$H = 3\sum_i \sigma_i^2 - \frac{1}{2} \sum_{|i-j|=1} \sigma_i^2 \sigma_j^2 \tag{6.11}$$

To facilitate the analysis of the system in finite domains Λ, let us rewrite the Hamiltonian as

$$H_\Lambda = \frac{1}{2} \sum_{\substack{i,j\in\Lambda \\ |i-j|=1}} \left(\sigma_i^2 - \sigma_j^2\right)^2 + \frac{1}{2} \sum_{i\in\Lambda} \sigma_i^2 \operatorname{card}\{ j \notin \Lambda \,|\, |j - i| = 1\} \tag{6.12}$$

The first term in (6.11) attains its absolute minimum on any configuration with $\sigma_i^2 = \text{const}$. Equation (6.12) clearly shows that for the "free" boundary conditions in (6.11) the only ground state is $\sigma_i \equiv 0$. As Griffiths pointed out, from this point of view the system has at least $2^{|\Lambda|}$ excitations with the low energy $\frac{1}{2}|\partial\Lambda|$, corresponding to configurations on which $\sigma_i = \pm 1$, but not 0. Thus, he concluded, $S_0 \geqslant \ln 2$, despite the nondegeneracy in finite volumes (for the above "free" boundary conditions).

Our approach permits us to discard the second term in (6.12) [which has no effect on $S(E)$ in the thermodynamic limit]. . We then have a case where all the pair energies can be minimized simultaneously. Following, mutatis mutandis, the analysis of Example 5, we conclude that the restricted set of ground state configurations $\hat{G}$ consists of all those for which $\sigma_i = \pm 1$, but not 0, and the one where $\sigma_i \equiv 0$. Thus $S_0 = \ln 2$, i.e., the lower bound described by Griffiths gives the full value of S_0.

There are other spectacular examples of lattice models which have $S_0 \neq 0$. One is the $d = 2$, triangular Ising antiferromagnet. Wannier[11] studied it in detail and calculated S_0 by explicitly calculating the limit in (1.4). By counting some of the ground state configurations (using an argument which he attributes to Anderson), Wannier found an entropy lower bound which was lower than S_0, as it should be. The point of our paper is that S_0 can really be computed by this direct route, even though the calculation is not an elementary matter.

Other examples for which $S_0 \neq 0$ can be calculated are the dimer systems[17,18] and the ice models.[19] The latter, having been proposed by Pauling[16] to account for the observed residual entropy of ice, must be considered to be one of the more successful applications of statistical mechanics to the real world.[15] Our point, once again, is that calculating the ground state configurational degeneracy is legitimate.

All these models also illustrate another important point. By choosing particular boundary conditions one can actually construct states for which the entropy is less than S_0, in fact zero. At first sight this might be considered conceptually puzzling, because if the ground state degeneracy is the only important quantity for S_0, then which one should be used? Answer: the maximal degeneracy.

As a final remark, let us remind the reader that in many models the set of parameters (of the Hamiltonian) on which the third law is violated forms a submanifold of lower dimension. A good general result in this direction still remains to be proven. A somewhat easier open problem is to decide whether the set of interactions of any given finite range for which $S_0 = 0$ is open.

ACKNOWLEDGMENT

We thank W. Thirring for stimulating discussions.

REFERENCES

1. R. B. Griffiths, *J. Math. Phys.* **6**:1447 (1965).
2. R. B. Griffiths, in *A Critical Review of Thermodynamics*, E. B. Stuart, B. Gal-Or, and A. J. Brainard, eds. (Mono Book Corp., Baltimore, 1970).
3. H. B. G. Casimir, *Z. Physik* **171**:246 (1963); M. J. Klein, in *Termodinamica Dei Processi Irreversibili*, S. R. De Groot, ed. (N. Zamichelli, Bologna, 1960), p. 1.
4. H. S. Leff, *Phys. Rev. A* **2**:2368 (1970).
5. J. Slawny, *Comm. Math. Phys.* **34**:271 (1973); **46**:75 (1976).
6. D. Ruelle, *Statistical Mechanics* (W. A. Benjamin, New York, 1969).
7. A. Wehrl, *Rev. Mod. Phys.* **50**:221 (1978).
8. R. Israel, *Convexity in the Theory of Lattice Gases* (Princeton Univ. Press, 1979).
9. R. L. Dobrushin, *Theor. Prob. Appl.* **13**:197 (1968); O. E. Lanford III and D. Ruelle, *Comm. Math. Phys.* **13**:194 (1969).
10. E. H. Lieb and J. L. Lebowitz, *Adv. Math.* **9**:316 (1972), p. 351.
11. G. H. Wannier, *Phys. Rev.* **79**:357 (1950).
12. M. Aizenman, E. B. Davies, and E. H. Lieb, *Adv. Math.* **28**:84 (1978).
13. E. B. Davies, *Quantum Theory of Open Systems* (Academic Press, New York, 1976).
14. J. Slawny, private communication.
15. W. F. Giauque and M. A. Ashley, *Phys. Rev.* **43**:81 (1933); W. F. Giauque and J. W. Stout, *J. Am. Chem. Soc.*, **58**:1144 (1936).
16. L. Pauling, *J. Am. Chem. Soc.* **57**:2680 (1935).
17. P. W. Kasteleyn, *Physica* **27**:1209 (1962).
18. H. N. V. Temperley and M. E. Fisher, *Phil. Mag.* **6**:1061 (1961).
19. E. H. Lieb, *Phys. Rev. Lett.* **18**:692 (1967); *Phys. Rev.* **162**:162 (1967).