Modern Physics Letters B Vol. 1 Nos. 1&2 (1987) 61–66

THE THIRD LAW OF THERMODYNAMICS*

JACEK MIĘKISZ and CHARLES RADIN

Mathematics Department, University of Texas, Austin, TX 78712 USA

Received 9 February 1987

We consider a very general class of discrete classical one dimensional statistical mechanical models and prove that generic finite range interactions have crystalline zero temperature ensembles, and in particular satisfy the third law of thermodynamics.

Most of our understanding of the solid state relies on the experimental fact that, at low temperature, matter strongly tends to ordered configurations at the molecular level[1]. The old problem of deducing this tendency from statistical mechanics[2–5] (which amounts to somewhat more than deriving the third law of thermodynamics) has only recently begun to yield to attack[6–26]. We will derive below the fact that, at least in one dimension, this ordering occurs for generic interactions.

We will consider rather general classical discrete alloy models (which can also be thought of as spin models) in one dimension, with finite range translation invariant interaction, and we will prove that generically such models are crystalline at zero temperature—in particular they satisfy the third law of thermodynamics.

Specifically, the models we consider are the following. At each integer site $j = 0, \pm 1, \pm 2, \ldots$, we have a classical occupation variable w_j which can assume any one of N possible values ($N \geq 2$ is fixed from here on) corresponding to the N possible molecular species which can occupy the site j. We allow many-body interactions of range R as follows. To each finite set S of sites with occupation values $w(S) = \{w_j, j \text{ in } S\}$ we assign a many-body energy $E(w(S))$. This function is assumed translation invariant. The total energy of a configuration $w = w([-n, n]) = \{w_{-n}, \ldots, w_n\}$ of the sites $j = 0, \pm 1, \ldots, \pm n$ is $E(w) = \sum_{S \subset [-n,n]} E(w(S))$. The finite range condition is just that $E(w(S)) = 0$ if the diameter of S is larger than R. (Note that one gets a two-body interaction if also $E(w(S)) = 0$ whenever S contains more than two sites).

*Supported in part by NSF Grant No. DMS-8501911

Our main construction[27] is that of a graph G which has N^{R+1} vertices, one for each possible configuration of $R + 1$ sites. Given two such vertices, V and V', corresponding to $\{w_1, \ldots, w_{R+1}\}$ and $\{w'_1, \ldots, w'_{R+1}\}$, there is an ordered edge in G from V to V' if and only if $w'_j = w_{j+1}, j = 1, \ldots, R$. The edge from V to V' is denoted (V, V') and the set of all ordered edges in G by G_E. Note that G has the special property T: If $(V, V'') \in G_E$, $(V', V'') \in G_E$ and $(V, V''') \in G_E$ then $(V', V''') \in G_E$.

We shall call a nonempty ordered set $L = \{V_1, \ldots, V_k\}$ of vertices of G a loop if $(V_j, V_{j+1}) \in G_E$ for $1 \leq j < k$ and $(V_k, V_1) \in G_E$. We denote the number of vertices in the loop L by $|L|$. The loop $L = \{V_1, \ldots, V_k\}$ is called an atom if for any partition of $\{V_1, \ldots, V_k\}$ into two nonempty ordered sets $\{V_{j_1}, \ldots, V_{j_n}\}$ and $\{V_{k_1}, \ldots, V_{k_m}\}$, where $j_r < j_{r+1}, r = 1, \ldots, n - 1$ and $k_p < k_{p+1}, p = 1, \ldots, m - 1$, either $\{V_{j_1}, \ldots, V_{j_n}\}$ and/or $\{V_{k_1}, \ldots, V_{k_m}\}$ is not a loop.

From property T we get immediately

Lemma 1. Let $\{V_1, \ldots, V_k\}$ be a loop.

a) If $(V_r, V_j) \in G_E$ and $j \leq r$, then $\{V_j, \ldots, V_r\}$ and $\{V_1, \ldots, V_{j-1}, V_{r+1}, \ldots, V_k\}$ are loops.

b) If $(V_j, V_r) \in G_E$ and $j \leq r - 2$, then $\{V_{j+1}, \ldots, V_{r-1}\}$ and $\{V_1, \ldots, V_j, V_r, \ldots, V_k\}$ are loops.

A corollary of b) is that all vertices in an atom are distinct.

From the definition of atoms it follows that every loop can be partitioned into atoms, though not necessarily uniquely.

Given an interaction of range R we associate the following energies with each vertex $V = \{w_1, \ldots, w_{R+1}\}$ and loop $L = \{V_1, \ldots, V_k\}$ of G

$$E(V) = \sum_{\substack{S \subset [1, R+1] \\ S \ni 1}} E(w(S)), \quad E(L) = \sum_{j=1}^{k} E(V_j).$$

If w is a configuration of all sites j, $-\infty < j < \infty$, we say it is periodic, and k is a period, if $w_{j+k} = w_j$ for all j. The energy density $e(w)$ of w is then

$$e(w) = \lim_{n \to \infty} \frac{1}{n} \sum_{S \subset [1, n]} E(w(S)).$$

We put this in a more convenient form as follows. First we associate the loop L_w with w by defining $V_1(w) = \{w_1, \ldots, w_{R+1}\}$, $V_2(w) = \{w_2, \ldots, w_{R+2}\}$, $\ldots$, $V_k(w) = \{w_k, \ldots, w_{k+R}\}$ and $L_w = \{V_1(w), \ldots, v_k(w)\}$. Then it is easily seen that

$$e(w) = \frac{1}{k} \sum_{j=1}^{k} E(V_j(w)) = \frac{1}{|L_w|} E(L_w).$$

Let $L_w = \bigcup_a A_a$ be a partition of L_w into atoms and note that

$$e(w) = \sum_a \frac{E(A_a)}{|A_a|} \frac{|A_a|}{|L_w|},$$

i.e. the energy density of w is a convex combination of that of the atoms. Since there are a finite number of possible atoms and each atom L gives rise to a periodic configuration w (for which $L_w = L$) it follows immediately that

Theorem 1. For any (finite range) interaction the energy density, as a function on periodic configurations, attains an absolute minimum.

This fact was first proven several years ago[27,16] after which examples were given[18] showing that the result fails even for some nearest neighbor models in two dimensions. Our next goal is to combine this theorem with a result on nondegeneracy (which will only hold generically, not for all interactions) to obtain a very strong result about equilibrium at zero temperature.

The set of interactions of range R has a finite number of real parameters, one for each ordered set

$$\{w_1, \ldots, w_k\}, 1 \leq k \leq R + 1, w_j = 1, \ldots, N.$$

The set of interactions is thus of the form $\mathbb{R}^m$ for some m. Generically these m energies will be rationally independent, i.e. will not lie on one of the countably many hyperplanes in $\mathbb{R}^m$, containing the origin, whose unit normal has rational coordinates. (By "generically" we include any of the usual interpretations, such as having complement of measure zero, or containing a countable intersection of dense open sets.) It follows that for a generic interaction two atoms have the same energy if and only if they are translates of each other, so there is a periodic configuration, unique up to translation, with minimum energy density. (Minimum here means minimum among all possible periodic configurations; an argument due to Sinai[28,17] however shows that no lower energy density can then be achieved by any nonperiodic configuration.) Unfortunately the existence of a unique periodic configuration with minimum energy density does not of itself determine the nature of the zero temperature structure, as shown by a recent preprint[24]. What we must do next therefore is draw some further consequences from our situation. For the rest of our argument we assume we are working with one of our generic interactions.

Let $e = e(\tilde{w})$ be the energy density of the unique (up to translation) periodic ground state configuration $\tilde{w}$. Let w^n be any sequence of periodic configurations whose energy densities $e_n = e(w^n)$ converge to e as $n \to \infty$. And let d_n be the density in w^n of all vertices which do not occur in the atom $L_{\tilde{w}}$.

Lemma 2. $d_n \to 0$ as $n \to \infty$.

Proof by contradiction. Assume that $\hat{w}^n = w^{i_n}$ is a subsequence of w^n with $d_{i_n} \geq d$ for some $d > 0$. We will show that $e_{i_n} \not\to e$. Let $L_{\hat{w}^n} = \{V_1, \ldots, V_{r_n}\}$. Among $V_1, \ldots, V_{r_n}$ there are $d_n r_n \geq d r_n$ vertices which do not occur in $L_{\tilde{w}}$. $L_{\hat{w}^n}$ can be partitioned into atoms. We denote by b_n the total number of vertices in atoms different from $L_{\tilde{w}}$ in this partition. Then

$$e_{i_n} \geq \frac{b_n(e + g) + (r_n - b_n)e}{r_n} = \frac{b_n g}{r_n} + e \geq e + dg,$$

where g is the minimum difference between the energy density of $L_{\tilde{w}}$ and all other atoms (besides translates). This proves the lemma.

Now let C be a "coloring" of diameter D, i.e. the restriction of some configuration to a finite subset (of diameter S) called the support of C. Translating the support of C, define f and f_n to be the densities with which C appears in $\tilde{w}$ and w^n respectively.

Lemma 3. $f_n \to f$ as $n \to \infty$.

Proof. Fix $\varepsilon > 0$, and choose M such that for $n > M$, $d_n < \varepsilon/(r + D)$ where r and r_n are the minimal periods of $\tilde{w}$ and w^n respectively. Consider the interval I of rr_n consecutive sites $1, 2, \ldots, rr_n$, and all translations of the support of the coloring C for which the leftmost site is in I. For any periodic configuration w let $N(w)$ be the number of times these translates of C appear in w. Clearly $N(\tilde{w}) = frr_n$. Now for each configuration w^n and each lattice site j we associate the vertex $V_j^n = \{w_j^n, \ldots, w_{j+R+1}^n\}$. Let V_i^n and V_j^n, $i < j$, be two vertices in $\{V_1^n, \ldots, V_{rr_n}^n\}$ which do not occur in $L_{\tilde{w}}$, and are also such that every V_k^n, $i < k < j$, does occur in $L_{\tilde{w}}$. These V_k^n's may form many copies of the atom $L_{\tilde{w}}$. Let $m \geq 0$ be the number of such consecutive atoms $L_{\tilde{w}}$ such that the distance between the last vertex of the last of these atoms and V_j^n is larger than D. Therefore the coloring C appears fmr times in w^n with leftmost end of its support at these mr sites. This gives us the bounds

$$f_n > \frac{rr_n f - (r + D)d_n rr_n}{rr_n}$$

$$f_n < \frac{rr_n f + (r + D)d_n rr_n}{rr_n},$$

i.e. $|f - f_n| < d_n(r + D)$, and therefore from lemma 2, $f_n \to f$ as $n \to \infty$.

We now wish to use lemma 3 to get further information about the zero temperature ensemble of our interaction. Technically, this ensemble is a probability measure, on the set of all periodic and nonperiodic configurations, obtained as follows. At finite temperature t one defines a possibly nonunique probability measure m_t as the infinite volume limit of the grand canonical ensemble, the N chemical potentials being the one-body terms in the interaction. By a zero temperature ensemble we mean any weak accumulation point of these m_t as $t \to 0$. From Theorem 2 in Ref. 21 it follows that there is exactly one translation invariant zero temperature ensemble and also, with the existence of our periodic ground state configuration $\tilde{w}$, that the average $\langle f \rangle$ of any continuous function f in the ensemble can be computed as

$$\langle f \rangle = \frac{1}{r} \sum_{j=1}^{r} f(T^j \tilde{w}),$$

where T is space translation by one unit and r is the period of $\tilde{w}$. This proves that our zero temperature ensemble is crystalline in the strongest possible sense.

In conclusion we have proven that for these rather general discrete one dimensional models

Theorem 2. For generic finite range interactions there is a unique translation invariant zero temperature grand canonical ensemble in the infinite volume limit. Furthermore the ensemble is just the average, over a unit cell, of a periodic configuration.

Now although it is a delicate matter in general to compute the entropy at zero temperature, in the ideal situation obtaining from Theorem 2 it follows[29] immediately that

Corollary. For generic finite range interactions the third law of thermodynamics holds.

Acknowledgement

It is a pleasure to acknowledge useful conversations with Bruce Palka.

References

1. P. W. Anderson, *Basic Notions of Condensed Matter Physics* (Benjamin/Cummings, Menlo Park, 1984).
2. S. G. Brush, *Statistical Physics and the Atomic Theory of Matter* (Princeton University Press, Princeton, 1983) p. 277.
3. B. Simon, *Perspectives in Mathematics: Anniversary of Oberwolfach 1984* (Birkhauser Verlag, Basel, 1984) pp. 442–443.
4. G. E. Uhlenbeck, *Fundamental Problems in Statistical Mechanics II*, ed. E. G. D. Cohen (Wiley, New York, 1968) p. 16.
5. G. E. Uhlenbeck, *Statistical Mechanics: Foundations and Applications*, ed. T. A. Bak (Benjamin, New York, 1967) p. 581.
6. W. J. Ventevogel, *Physica (Utrecht)* **92A** (1978) 343.
7. W. J. Ventevogel and B. R. A. Nijboer, *Physica (Utrecht)* **98A** (1979) 274.
8. W. J. Ventevogel and B. R. A. Nijboer, *Physica (Utrecht)* **99A** (1979) 569.
9. C. S. Gardner and C. Radin, *J. Stat. Phys.* **20** (1979) 719.
10. G. C. Hamrick and C. Radin, *J. Stat. Phys.* **21** (1979) 601.
11. R. C. Heitmann and C. Radin, *J. Stat. Phys.* **22** (1980) 281.
12. B. Borden and C. Radin, *J. Chem. Phys.* **75** (1981) 2012.
13. C. Radin, *J. Stat. Phys.* **26** (1981) 365.
14. C. Radin, *Physica (Utrecht)* **113A** (1982) 338.
15. F. Nicolò and C. Radin, *J. Stat. Phys.* **28** (1982) 473.
16. C. Radin and L. Schulman, *Phys. Rev. Lett.* **51** (1983) 621.
17. C. Radin, *J. Stat. Phys.* **35** (1984) 109.
18. C. Radin, *J. Math. Phys.* **26** (1985) 1342.
19. C. Radin, *Phys. Lett.* **A114** (1986) 381.

20. C. Radin, *Commun. Math. Phys.* **105** (1986) 385.
21. C. Radin, *J. Stat. Phys.* **43** (1986) 707.
22. J. Miękisz and C. Radin, *Phys. Lett.* **A119** (1986) 133.
23. J. Miękisz, *Commun. Math. Phys.* **107** (1986) 577.
24. J. Miękisz, "Classical Lattice Gas Model with a Unique Nondegenerate but Unstable Periodic Ground State Configuration", *Commun. Math. Phys.*, to appear.
25. B. R. A. Nijboer and T. W. Ruijgrok, *J. Phys. C: Solid State Phys.* **18** (1985) 2043.
26. B. R. A. Nijboer and T. W. Ruijgrok, *Physica (Utrecht)* **133A** (1985) 319.
27. M. Bundaru, N. Angelescu and G. Nenciu, *Phys. Lett.* **43A** (1973) 5.
28. Ya. G. Sinai, *Theory of Phase Transitions: Rigorous Results* (Pergamon, New York, 1982) p. 36.
29. M. Aizenman and E. Lieb, *J. Stat. Phys.* **24** (1981) 279.