Why solids are not really crystalline

Jacek Miękisz and Charles Radin
Department of Mathematics, University of Texas, Austin, Texas 78712
(Received 26 August 1988)

Working with lattice-gas models, we give evidence that even at zero temperature matter does not always tend to form crystals; unit cells may tend to go out of phase. In particular, our results imply that noncrystalline equilibrium materials such as quasicrystals and incommensurate solids are not aberrations, but rather should be expected.

The conventional intuitive understanding of the crystalline state of matter is based on perturbation about zero temperature, namely, it is argued that at zero temperature minimization of the free energy can *only* be obtained with a periodic arrangement of particles (a perfect crystal) which at nonzero temperature is disrupted by defects due to entropy. We will show below that this intuitive picture is wrong for the following surprising reason: (at least) among classical lattice-gas models, for most (i.e., generic) interactions even at zero temperature the minimum free-energy arrangement *cannot* in fact be periodic, i.e., is not crystalline. Since such models are known to be physically reasonable for at least some materials, this shows that one should not view noncrystalline equilibrium solids, such as quasicrystals and incommensurates, as in any sense unnatural, but should in fact *expect* to find such materials.

Before going any further, we must make some tempering remarks about the notion of genericity. A subset of a topological space X (which we will assume is a complete metric space, or better yet a Banach space) is said to be generic if it contains a countable intersection of dense open subsets of X. Note that a countable intersection of generic sets must again be generic. One of the key facts about generic sets is that a generic set is automatically dense; this is a fundamental result due to Baire. These two facts together are the basis for using the property of genericity to characterize those sets containing "most" of the points of X. Now there are several other mathematical notions available, besides genericity, to make precise the intuitive notion that a set contains most points. In a finite-dimensional Euclidean space one of the best known is that the set has complement of (Lebesgue) measure zero. However there are simple examples of sets that are generic but of measure zero, so these two notions of largeness (and other common ones such as dimension) are by no means the same. If one is using such a notion to gain information or intuition, such information follows *only to the extent that the notion is appropriate.* In finite-dimensional Euclidean space it is more common to use the measure theoretical notion if there is a *natural* probability measure around, since this makes clear in what sense the points in the complement of the "large" set can be neglected. However in infinite-dimensional spaces there is rarely a measure available which can play this role. To be specific, for us the space X will be the space of all allowed interactions for a lattice-gas model, and there does not seem to be any *natural* measure on X which can be used to define largeness. In such a situation mathematicians have found that genericity is often the best of bad alternatives and it is with this note of caution that we use the idea of genericity. (See Ref. 1 for a good mathematical introduction to genericity.) To summarize, we assume that the behavior of generic interactions is *evidence* of the behavior of typical interactions; by no means is it convincing *proof* that typical physical interactions behave in that manner.

The attempt to deduce, within statistical mechanics, the basic mechanism which forces matter to be crystalline at low temperature is of course an old and highly venerated problem.[2-6] There has been a concerted attack on the problem in the last decade[7-31] (see Ref. 26 for a detailed history), and the best result to date is a recent proof[27] that for most (i.e., generic) interactions the ground state at least exhibits long-range order (again, among classical lattice-gas models). We will use similar techniques to show that these ordered ground states are not perfectly ordered, i.e., not strictly periodic. It remains unresolved precisely what a typical ground state, which has long-range order but is not fully ordered, in fact looks like; needless to say, such states may be hard to distinguish from perfectly periodic ones.

In classical lattice-gas models one considers a field, ϕ, on, say, the three-dimensional simple-cubic lattice, $\mathbb{Z}^3$, with finitely many possible values at each lattice site, each value interpreted as the occupation status of the site; one value, e, is reserved to mean "empty" and the others represent different internal states of a single particle. We will refer to a set of field variables for all sites as a "configuration." By a "ground-state distribution" we mean a limit, as temperature goes to zero, of the translation-invariant grand canonical probability distribution on the set of all configurations, and by a "ground-state configuration" we mean any configuration in the support of the ground-state distribution. The (two-body, translation-invariant) interaction between state a at site $\mathbf{x}$ and state b at site $\mathbf{x}+\mathbf{y}$ will be denoted $V(a,b;\mathbf{y})$; if $\mathbf{y}=\mathbf{0}$, this vanishes if either $a\neq b$ or both a and b represent

 ©1989 The American Physical Society

empty, and otherwise it represents the (negative of) the chemical potential. We only allow those interactions V for which

$$\|V\| \equiv \sum_{\mathbf{y}\in \mathbb{Z}^3} \sum_{a,b} |V(a,b;\mathbf{y})| < \infty$$

thereby defining a norm on the space of interactions. (We will have more to say about this norm near the end of this paper.) To make the lattice approximation convincing one should have many lattice spacings within a typical interparticle separation, and to ensure this it is common to add an "extended-hard-core" condition to the model, namely, to require that in all (allowed) configurations no two particles are allowed closer together than some fixed multiple $M>1$ of the lattice spacing; for simplicity we will assume $M=2^{1/2}$. For any configuration ϕ and interaction V let $e_V(\phi)$ be the energy per site in ϕ (assuming it exists). Note that $e_{V+U}(\phi)=e_V(\phi)+e_U(\phi)$ and $|e_V(\phi)| \le \|V\|$, for any V, U, and ϕ. Let W be an interaction of finite range r, i.e., $W(a,b;\mathbf{x})=0$ if $|x|>r$. (Note that the set of all finite-range interactions is dense in the space of all interactions.) Let $\mathbf{x}_1$, $\mathbf{x}_2$, and $\mathbf{x}_3$ be the usual basis in $\mathbb{Z}^3$, and for each positive integer n let Θ^{a_n} be the interaction:

$$\Theta^{a_n}(a,b;\mathbf{x}) = \begin{cases} -a_n^{-1/2}, & \text{if } \mathbf{x}=a_n\mathbf{x}_j \text{ for some } j, \text{ and } a=b \\ 0, & \text{otherwise} \end{cases}$$

where $a_n=[3n(W)]^2(n+5)!$ and $n(W)$ is the smallest integer larger than $(r+1)\|W\|$. So for fixed interaction W of finite range r, and with this definition of a_n (which must be a multiple of $n!$ in order to account for all possible periods less than n) we have the following.

Lemma. If $\|V-(W-\Theta^{a_n})\| < (r+1)\|W\|/a_n$ then the only periodic ground-state configuration which V can have, of period less than n along all three axes, is the vacuum.

Proof. Assume otherwise, and call the periodic ground-state configuration, of period $m<n$, ϕ. Let ϕ_j be the translate of ϕ by $\mathbf{x}_j$, and note that by assumption ϕ and ϕ_j must differ in every unit cell of ϕ for some $j=1$, 2, or 3; without loss of generality assume this occurs for $j=1$. Define the periodic configuration $\tilde{\phi}$ by

$$\begin{aligned} \tilde{\phi}(\mathbf{x}) &= \phi(\mathbf{x}) \quad \text{if } 2ka_n < x_1 < (2k+1)a_n \\ &= \phi_1(\mathbf{x}) \quad \text{if } (2k+1)a_n < x_1 < (2k+2)a_n \\ &= e \quad \text{if } x_1=(2k+1)a_n \text{ or } (2k+2)a_n \end{aligned}$$

for all integers k. Basically, $\tilde{\phi}$ consists of alternating strips of ϕ and the translate ϕ_1 of ϕ, with particles eliminated at the edges of the strips to satisfy the hard-core exclusion. Then

$$\begin{aligned} e_V(\tilde{\phi}) &= e_{W-\Theta^{a_n}}(\tilde{\phi}) + e_{V-W+\Theta^{a_n}}(\tilde{\phi}) \le [e_{W-\Theta^{a_n}}(\phi)+(r+1)\|W\|/a_n] - m^{-3}a_n^{-1/2} + (r+1)\|W\|/a_n \\ &\le e_{W-\Theta^{a_n}}(\phi) + 2(r+1)\|W\|/a_n - n^{-3}a_n^{-1/2} \\ &\le e_V(\phi) + e_{W-\Theta^{a_n}-V}(\phi) + 2(r+1)\|W\|/a_n - n^{-3}a_n^{-1/2} \\ &\le e_V(\phi) + 3(r+1)\|W\|/a_n - n^{-3}a_n^{-1/2} < e_V(\phi) , \end{aligned}$$

where the term in brackets is an estimate of the energy cost at the edges of the strips: $r\|W\|$ counting all possible interactions through W across the edges of the strips, the additional $\|W\|$ due to eliminated particles at the edges, and the m^{-3} term due to Θ^{a_n} since there is at least one particle in each unit cell of ϕ which is no longer interacting through Θ^{a_n} across the edges of the strips. Since ϕ is a ground state $e_V(\phi)$ cannot be greater than $e_V(\psi)$ for any ψ, and this proves the lemma.

Now define, for each positive integer k,

$$B_k = \bigcup_W \bigcup_{n\ge k} \{V \mid \|V-(W-\Theta^{a_n})\| < (r+1)\|W\|/a_n\}$$

and $B=\bigcap_{k\ge 1} B_k$. Note that each B_k is open and dense in the Banach space of interactions, and therefore B is generic[1]—i.e., it contains most interactions. If V belongs to B there exists, for each $k\ge 1$, W_k of range r_k and $n\ge k$ such that $\|V-(W_k-\Theta^{a_n})\| < (r_k+1)\|W_k\|/a_n$, so the lemma is applicable. Since this is true for all k we conclude that the only periodic ground-state configuration that V can have is the vacuum. We summarize our results as follows.

Theorem. For most interactions with extended hard core (i.e., generically), *no* ground-state configuration is periodic unless it is the vacuum.

Remarks. (1) Since genericity implies denseness, we see that for *any* interaction there is a perturbation of it, as small as desired, for which the only periodic ground state possible is the vacuum. (2) The theorem is only of interest if the norm we are using is reasonable. We note the following in this regard. First, it is the most commonly used norm in mathematical proofs of the qualitative behavior of many-body systems (see, for example, Ref. 32) because it corresponds to the restriction that the sum, of the energies of interaction of any fixed particle with all other particles, be finite. In particular, among spherically symmetric interactions this requires that the interactions fall off faster than $1/r^3$, so it is roughly a restriction to short range. On the other hand, the interactions which appear in the proof (which appear to have long range but of course do not—they are merely highly directional) may not give the correct physical mechanism; one reason to suspect this is that there are *nearest-neighbor* models[18–20,22,23,25] which have noncrystalline ground states, of special interest to the study of quasicrystals[26] since they are based on examples of nonperiodic tiling models, and these models do not seem to be predicted by the proof.

This result together with that of Ref. 27 gives a new picture of what a ground state must look like—it has long-range order from Ref. 27, but not the perfect order of true periodicity. Unfortunately it is still not clear how to characterize, geometrically, how these nonperiodic ground-state configurations should appear although from the above argument it seems that large blocks of unit cells tend to go out of phase with one another.

In conclusion we note that our basic result, that the noncrystalline ground states of materials such as quasicrystals and incommensurate solids are not aberrations but quite natural, should lead to a better understanding of all solids.

This research was supported in part by NSF Grant No. DMS-8701616.

[1] J. C. Oxtoby, *Measure and Category* (Springer-Verlag, New York, 1971).

[2] P. W. Anderson, *Basic Notions of Condensed Matter Physics* (Benjamin, Menlo Park, 1984), p. 12.

[3] S. G. Brush, *Statistical Physics and the Atomic Theory of Matter, from Boyle and Newton to Landau and Onsager* (Princeton University Press, Princeton, 1983), p. 277.

[4] B. Simon, in *Perspectives in Mathematics: Anniversary of Oberwolfach 1984* (Birkhauser-Verlag, Basel, 1984), p. 442.

[5] G. E. Uhlenbeck, in *Fundamental Problems in Statistical Mechanics II,* edited by E. G. D. Cohen (Wiley, New York, 1968), p. 16.

[6] G. E. Uhlenbeck, in *Statistical Mechanics; Foundations and Applications,* edited by T. A. Bak (Benjamin, New York, 1967), p. 581.

[7] W. J. Ventevogel, Physica A **92**, 343 (1978).

[8] W. J. Ventevogel and B. R. A. Nijboer, Physica A **98**, 274 (1979).

[9] W. J. Ventevogel and B. R. A. Nijboer, Physica A **99**, 569 (1979).

[10] C. S. Gardner and C. Radin, J. Stat. Phys. **20**, 719 (1979).

[11] G. C. Hamrick and C. Radin, J. Stat. Phys. **21**, 601 (1979).

[12] R. C. Heitmann and C. Radin, J. Stat. Phys. **22**, 281 (1980).

[13] B. Borden and C. Radin, J. Chem. Phys. **75**, 2012 (1981).

[14] C. Radin, J. Stat. Phys. **26**, 365 (1981).

[15] F. Nicolò and C. Radin, J. Stat. Phys. **28**, 473 (1982).

[16] C. Radin and L. S. Schulman, Phys. Rev. Lett. **51**, 621 (1983).

[17] C. Radin, J. Stat. Phys. **35**, 109 (1984).

[18] C. Radin, J. Math. Phys. **26**, 1342 (1985).

[19] C. Radin, Phys. Lett. **114A**, 381 (1986).

[20] C. Radin, Commun. Math. Phys. **105**, 385 (1986).

[21] C. Radin, J. Stat. Phys. **43**, 707 (1986).

[22] J. Miękisz and C. Radin, Phys. Lett. **119A**, 133 (1986).

[23] J. Miękisz, Commun. Math. Phys. **107**, 577 (1986).

[24] J. Miękisz and C. Radin, Mod. Phys. Lett. B **1**, 61 (1987).

[25] J. Miękisz, Commun. Math. Phys. **111**, 533 (1987).

[26] C. Radin, Int. J. Mod. Phys. B **1**, 1157 (1987).

[27] J. Miękisz, J. Phys. A **21**, L529 (1988).

[28] B. R. A. Nijboer and Th. W. Ruijgrok, J. Phys. C **18**, 2043 (1985).

[29] B. R. A. Nijboer and Th. W. Ruijgrok, Physica A **133**, 319 (1985).

[30] M. Duneau and A. Katz, Ann. Inst. Henri Poincaré **37**, 249 (1982).

[31] A. Katz and M. Duneau, J. Stat. Phys. **29**, 475 (1982).

[32] D. Ruelle, *Statistical Mechanics; Rigorous Results* (Benjamin, New York, 1969).