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LOW TEMPERATURE AND THE ORIGIN OF CRYSTALLINE SYMMETRY*

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This is a status report on the classical problem of determining the origins of crystalline symmetry in low temperature matter.

1. The Crystal Problem: Physical Background

The problem we are addressing has many aspects, but we can capture the essence of it with the question: *Why are solids crystalline?* That is, precisely what are the fundamental (microscopic) mechanisms which force low temperature matter to be crystalline rather than, say, amorphous? In this section we shall explore some of the physics background for this "crystal problem".

First we note some well known experimental facts. At very low temperature, the only known (neutral, macroscopic) material which is not solid at atmospheric pressure is helium (either isotope), and helium is solid at high pressure. So restricting attention temporarily to "simple" substances, which by definition are parametrized in thermodynamic equilibrium by two (experimentally adjustable) intensive variables, say temperature, T, and pressure, P, (or T and chemical potential, which we denote by M instead of the more usual μ) we know that in general for fixed low T there is a range of values of P for which the substance is solid, and a range for which it is fluid. We are primarily interested in the solid phase — the interesting fact of its existence and, in particular, its microscopic periodicity.

Since a crystal just consists of some unit cell repeated periodically in three directions — see Fig. 1 — we take as given that we are trying to understand the reasons why microscopic physical-space periodicity *must* be present, for some range of T and P, in the partition function of any reasonable model of matter. We

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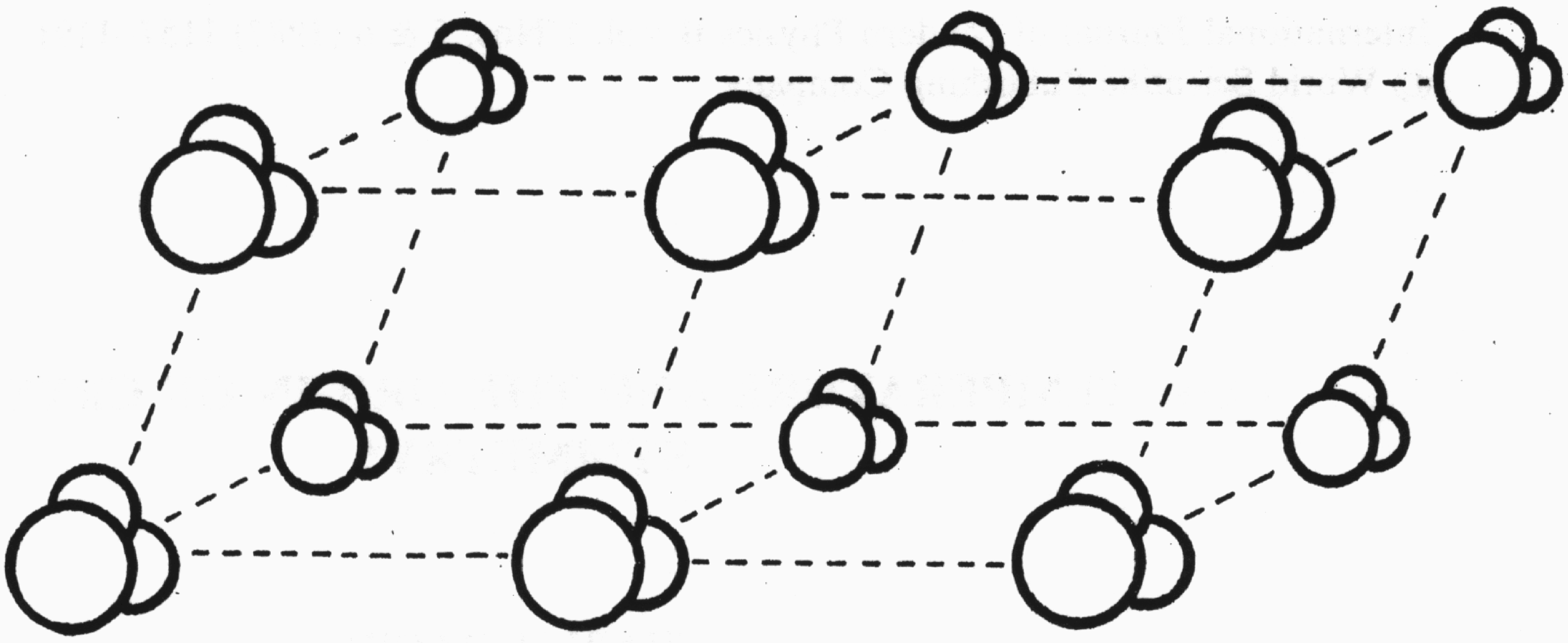


Fig. 1. Crystal with unit cell of three particles.

emphasize the word "must"; we do not just want to show that crystallinity is compatible, or possible, but is *forced.* And we want to understand the mechanisms doing the forcing.

It is natural to approach the problem in the following way. Given a large number, N, (say a million: argon clusters of the order of a thousand are in fact not crystalline[1] which indicates, by the way, limitations on computer simulation for our problem) of identical nuclei, each of charge q, and qN electrons, all interacting through static Coulomb forces, we should compute the n-point functions, $r(x_1, x_2, \ldots, x_n)$, which represent the relative probabilities of having particles at the n positions $x_1, \ldots, x_n$. Examination of the n-point functions should then solve the crystal problem. (This line of argument is discussed in detail below.)

The only quantum mechanical calculations of this sort we know of are the recent remarkable results of Fefferman[2,3], in which it is demonstrated that in one range of temperature and chemical potentials matter forms an ionized plasma, and in another range it forms a disordered neutral fluid (of atoms). His methods have not yet been applied to the solid regime.

Fortunately, simpler models are applicable for the specific purpose of the crystal problem. We know that an equilibrium state must minimize the Gibbs free energy per particle $f_G = (e + P - Ts)/d$ if P and T are fixed, (where e is the energy density — density being reserved to mean "per unit volume" — d the particle density and s the entropy density, and the state can be modeled by the pressure ensemble of statistical mechanics), or the Landau free energy density $f_L = e - Md - Ts$ if M and T are fixed, (and the state can be modeled by the grand canonical ensemble of statistical mechanics). For finite systems an extensive variable controls the size of the system; for this purpose volume is fixed in a grand canonical ensemble, and particle number is fixed in a pressure ensemble. At zero pressure and zero temperature the latter thus corresponds to minimizing the total energy. (Although this is only true at zero pressure and temperature we will occasionally neglect the pressure restriction when casually discussing the crystal problem.) Now at low temperature we expect from the Third Law of Thermodynamics (which says that entropy goes to zero with

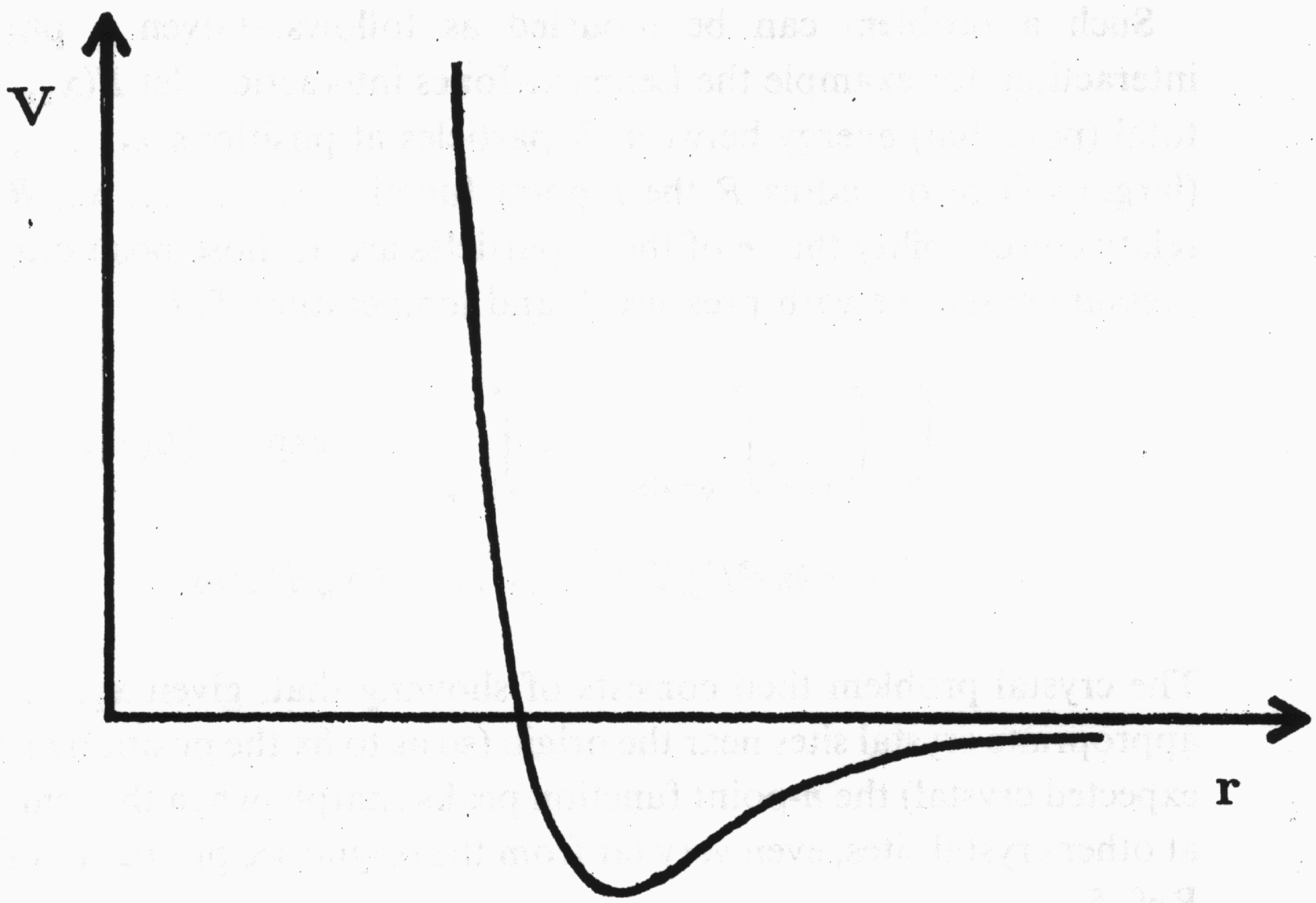


Fig. 2. Lennard-Jones' six-twelve potential: $V(r) = c_1r^{-12} - c_2r^{-6}$.

temperature) that the entropy contribution to the free energy is negligible, so a low free energy state is one with low $e - Md$ or low $(e + P)/d$. At these low temperatures we expect the nuclei and electrons to have formed molecules — Fefferman's work is the first convincing theoretical confirmation of this fundamental assumption — so that we are really just trying to determine the most probable arrangement of molecular positions. (This picture is most appropriate for van der Waals or ionic solids, in which all the constituent particles are roughly associated with individual molecules or ions, and less appropriate for metals.) Therefore if one uses a phenomenological force (say taken from experiments in the fluid state, such as the Lennard-Jones six-twelve law, $V(r) = c_1r^{-12} - c_2r^{-6}$ — see Fig. 2 — for argon) to model the interaction of the molecules, classical statistical mechanics should be reliable. (The "exception" of helium in this picture is usually "explained" by its unique combination of a very weak molecular interaction and a very low nuclear mass. We will say more about this below. Classical mechanical models of metallic solids which are convincing with respect to the crystal problem are perhaps less obvious, but there is no difference in principle.)

Using classical statistical mechanics then, our goal is to understand why a configuration of point particles, interacting through a reasonable force law, is *forced* to be periodic (i.e. crystalline) if it is to have minimum possible $(e + P)/d$ or $e - Md$. (Of course we will always assume translation invariant interactions; obtaining periodicity by means, say, of a periodic external field, would not be relevant.) To make this very specific, take the Lennard-Jones law. Then we are asking: *Why is the minimum energy configuration, for say a million interacting argon atoms, a* (piece of a hexagonal close packed) *crystal*?

Such a problem can be modeled as follows. Given a physically reasonable interaction, for example the Lennard-Jones interaction, let $E(x_1, \ldots, x_N)$ denote the total (potential) energy between N particles at positions $x_1, \ldots, x_N$. Then within a (large) sphere of radius R the n-point function $r(x_1, \ldots, x_n; R)$, representing the relative probability that n of the N particles are at those positions, is given, using the pressure ensemble with pressure P and temperature T, by

$$\int_0^R \int_{|x| \leq R} \int_{|x_N - x| \leq s} \cdots \int_{|x_{n+1} - x| \leq s} \exp - [E(x_1, \ldots, x_N) + P4\pi s^3/3]/T \, d^3 x_{n+1} \ldots d^3 x_N \, d^3 x \, ds.$$

The crystal problem then consists of showing that, given $x_1, \ldots, x_4$ fixed at some appropriate crystal sites near the origin (so as to fix the position and orientation of the expected crystal) the n-point function peaks sharply when the remaining positions are at other crystal sites, even very far from the origin; see pp. 16–17 of Ref. 4 and p. 46 of Ref. 5.

It is appropriate at this point to note how the above model changes to accommodate non-"simple" matter; in particular, we wish to emphasize alloys. Some alloys, for example brass, exhibit the following behavior — see Fig. 3. At very low temperatures they are ordinary crystals, and at high temperatures they are ordinary fluids, but in the solid phase the high temperature portion is disordered in the sense that the atomic species that occupy the crystal sites are not correlated over long distances (as they are in the low temperature, "ordinary crystal" phase). In other words, as one raises the temperature of such materials starting from the low end, at fixed chemical potentials, there is first an order-disorder transition (at which the site occupation becomes disordered), and then the melting transition (at which the positions of the sites themselves become disordered)[6]. Such materials are most easily modeled using a grand canonical ensemble rather than the pressure ensemble, and it is necessary to use separate chemical potentials for each of the (m possible) component species, and add an internal variable to the description of the point particles so as to distinguish the species. Therefore within a sphere of radius R the n-point function, representing the relative probability that the jth (out of n) particle is of species s_j and is located at position x_j, for all j from 1 to n, is given by

$$\sum_{k=n}^{\infty} \sum_{s_{n+1}=1}^{m} \cdots \sum_{s_k=1}^{m} \int_{|x_k| \leq R} \cdots \int_{|x_{n+1}| \leq R} [\exp - [E((x_1, s_1), \ldots, (x_k, s_k)) - M_1 n_1 - \ldots - M_m n_m]/T][1/(n_1! \ldots n_m!)] \, d^3 x_{n+1} \ldots d^3 x_k.$$

where n_j is the number of the k particles which are of species j.

Since relatively little in the way of (mathematically) exact work has been done with standard models of particles in three dimensions (we will refer to such models as used

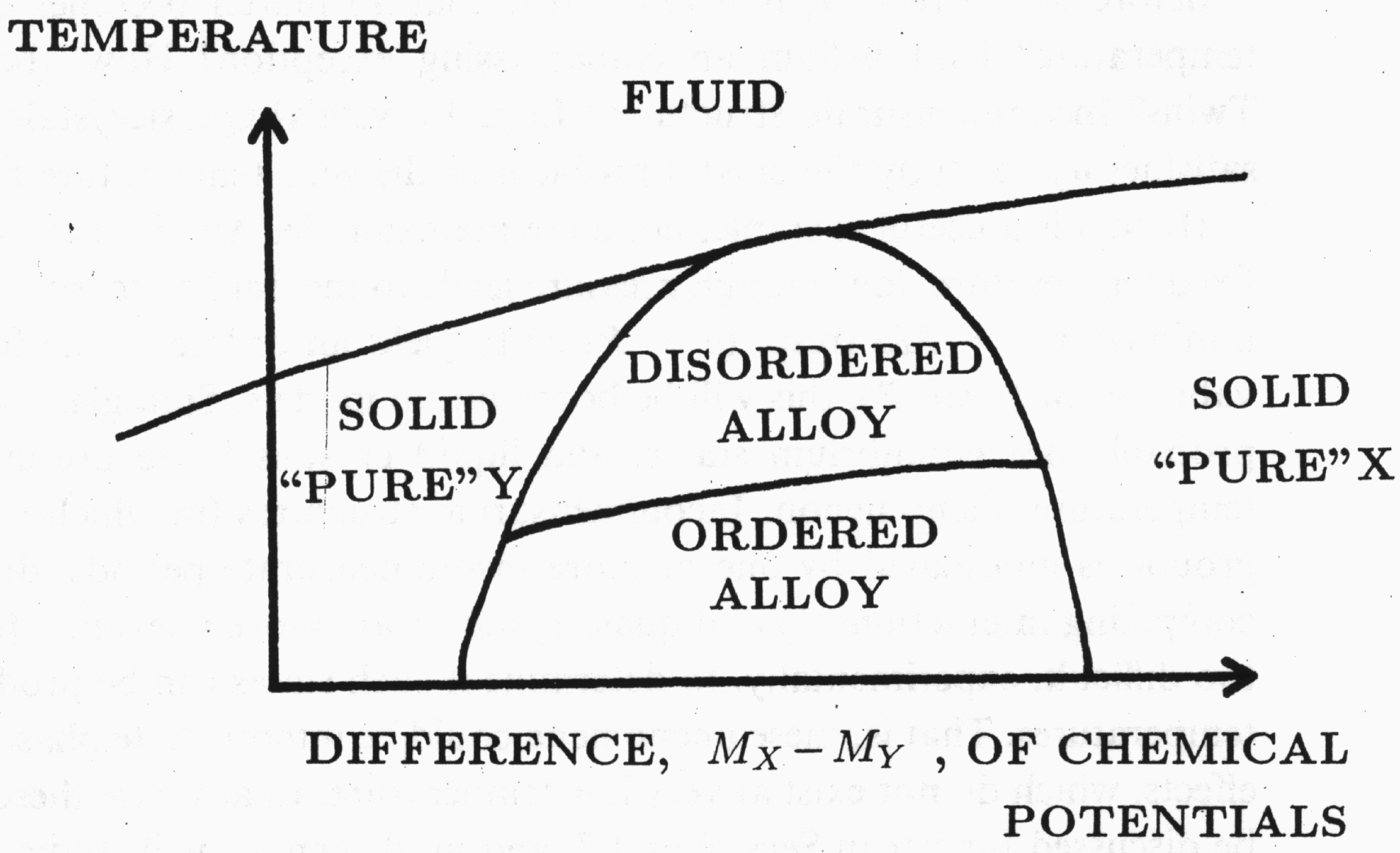


Fig. 3. A simplified phase diagram of a two component ($X - Y$) system.

above as "continuum models"), it will be useful to reformulate the crystal problem in terms of discrete models. We will use the term "alloy model" (in place of the more standard term "spin model") in more generality later, but for now we assume it refers to a ν-dimensional cubic lattice, $\mathbf{Z}^\nu$, a finite (internal-variable) set, S, and a finite range, translation invariant, two-body interaction, V. A "configuration" is an assignment of an element, s_j, of S for each point ("site"), j, of $\mathbf{Z}^\nu$. (s_j is thought of as the chemical species occupying j, which in effect implies there is a point hard core in V since at most one particle can occupy any given site. One of these values can be reserved to signify an empty site, in which case we refer to the model as a "lattice gas" model.) The statistical mechanics of the model just assigns relative probabilities to the possible configurations by means of the usual Gibbs factors; as above we use a grand canonical ensemble. Examples we will refer to later are the 2-dimensional, one component lattice gas models, with isotropic nearest neighbor attraction (which is related to the Ising ferromagnet) or with isotropic nearest neighbor repulsion (which is related to the Ising antiferromagnet).

It is natural to wonder whether alloy models, in which one has inserted a periodic structure by fiat, are at all relevant for the crystal problem. It is certainly true that entropy behaves differently between discrete and continuum models, so it is controversial to use discrete models to study melting.[7] But for the crystal problem, in which we just try to minimize $e - Md$ (and entropy does not appear), the use of discrete models is really less troubling. We know from the order-disorder transitions of alloys, as noted above, that periodicity of site occupation is not automatic, and is in fact in these situations more delicate (is more easily destroyed, "by heat") than the underlying crystal structure. Finally we will exhibit, in Sec. 6, toy models which prove that the assumption of an underlying lattice does not trivialize the problem.

Before we go further, is it really true that all matter becomes crystalline at low temperature? Isn't helium an embarrassing exception? How about spin glasses? Twins? Incommensurate structures? Liquid crystals? Quasicrystals? And is it really satisfactory to study the crystal problem in the zero temperature limit?

Helium is a useful example, not a counterexample. And in fact for any material at fixed temperature, low enough pressure leads to the fluid state, so we can only expect minimizing $e - Md$ (resp. $(e + P)/d$) to yield an ordered state for some range of values of M (resp. P); this will be borne out in models. Spin glasses[8] and twins [9] are probably not equilibrium states, and liquid crystals[10] are presumably not a low temperature phenomenon. Incommensurate structures (in which a crystalline background is modulated by one or more incommensurate periods, due presumably to competing interactions[11]) and quasicrystals[12] are more relevant. However it may be too difficult, experimentally, to determine if such states can be produced at very low temperatures. That is, these phenomena could be intermediate phases, due to entropy effects, which do not exist at very low temperature. In any case these phenomena will be discussed further in Secs. 6 and 7, and until then we will studiously ignore them.

As to taking the zero temperature limit, we note the following. Our basic problem is to understand why low (not zero) temperature leads to a crystalline minimum for any free energy, such as $(e + P - Ts)/d$; "any" refers here to any reasonable interaction. We expect that at intermediate temperatures there is a competition between $(e + P)/d$ and $-Ts/d$. The study of this competition is the study of phase transitions, such as melting, and folklore has it that on each side of the transition temperature one or the other of these two parts of the free energy is dominant. We know that at high temperature the latter (entropy) part is indeed dominant (that is, minimization of the free energy is attained by minimization of $-Ts/d$) and leads to a disordered gas; see p. 76 of Ref. 13. Since the Third Law of Thermodynamics implies that at low (not necessarily zero) temperature the former part, $(e + P)/d$, is dominant, we have isolated as the "crystal problem" the attempt to understand why minimizing $(e + P)/d$ leads to periodicity. So taking the zero temperature limit is actually part of the crystal problem. This is very important in determining the appropriateness of models, since it allows us to use models (in particular low dimensional models) in which the entropy-energy balance is unphysical.

In summary, there is a great body of experimental evidence, supported by our experience with mathematical models, which indicates that minimum energy configurations of many interacting particles have a strong tendency to be periodic. And yet, as we shall see in the next section, there is little or no understanding, even at the most intuitive level, of the underlying mechanism.

2. History of the Crystal Problem

We will only consider the history of the crystal problem in this century, and in the framework of Gibbs' statistical mechanics. (For an interesting discussion of earlier theories, see Ref. 14.) In fact the present day view, that all phases of matter including the solid should be calculable from a single partition function by varying the temperature and pressure, only dates from the late nineteen thirties; see p. 31 in Ref. 15 and p. 103 in Ref. 16.

The earliest relevant references we know of on the crystal problem are by Hermann Weyl: "... if equal atoms exert forces on each other that make possible a definite stable state of equilibrium for the atomic ensemble, then the atoms will of necessity arrange themselves in a regular system of points in our strict sense" — see p. 292 of Ref. 17. By "regular system of points" he means "a set lying in the same manner around each of its points"; *ibid.* p. 291. This discussion is repeated almost verbatim on p. 126 of Ref. 18. Unfortunately, Weyl does not explain his claim. In fact as stated it is certainly wrong since there are crytals, for example the low temperature phase of manganese (which has a unit cell of 58 atoms; see pp. 191ff of Ref. 19), which are not regular in this sense. This can also be seen in toy models as we shall see in Sec. 6. For example one can easily exhibit 1-dimensional models (of identical particles) whose ground states have a unit cell of three equally spaced particles; clearly the center particles of these unit cells have a different environment from that of the other particles. Two comments should be added to the above discussion. First there are occasional resurrections of this erroneous line of argument: see for example p. 241 in Ref. 20. And also, although Weyl does not reference his claim, it is tempting to view it as an erroneous amplification of the discussion in Secs. II.8 and II.9 in Ref. 21, with which Weyl was undoubtedly familiar.

Casual references to the crystal problem, as an unsolved problem, appear in the literature: see for example pp. 7–9 in Ref. 22. But the first serious discussion of the problem that we know of is due to Uhlenbeck (p. 581 in Ref. 23 and pp. 16–17 in Ref. 4) and is in large part the original source of our ideas in Sec. 1.

Another serious discussion appears in a remarkable book by Anderson,[24] which is a tour de force on the theme of symmetry in condensed matter physics. The crystal problem is naturally considered at some length (as a prototype) to understand the origin of symmetry caused by low temperature. Since the spirit of the argument is somewhat seductive, and is widely believed, it is worthwhile including it in our survey. First, to do the argument justice, and since Anderson's presentation is so clear, we quote it in full.

> So far as I know, there exists no proof that among the lowest energy configurations C at least one is a regular lattice, but I for one would be very surprised if this weren't so. One may work up a reasonable argument for it as follows: Let us take a relatively small box containing n atoms and consider its optimum configuration. There will be one minimum-energy configuration, all small displacements from which are described by a harmonic potential ... (incidentally, we may allow small changes in the shape of our box to minimize the energy further). The effect of the smallness of the box may be minimized by using periodic boundary conditions.
>
> For large displacements, however, there may be additional relative minima: for instance, but not typically, a single atom may have two possible potential wells within which it might sit, one lower than the other .... Such a second minimum will have an energy only of order unity above the true minimum; but in general the other configurations will typically have energies $\sim n$ higher (as in the regular case, lattice

> energy differences for different lattices are proportional to the size of the crystal; even for an irregular array moving every atom in an essential way will change the energy by $\sim n$).
>
> Now we imagine putting a much larger array together of $N = mn$ atoms. An attempt at a low-energy configuration may be made by simply piling all the boxes of n atoms together and removing the interior walls. We can expect that small harmonic readjustments will further improve the energy; but our basic argument is that the energy of misfit between the surfaces of the small pieces is a surface energy, of order $n^{2/3}$, while the energy necessary to change the interior configuration in an essential way will be $\sim n$, so that there will be a cell size, n, beyond which it will not pay to modify the internal configurations; this then gives us a regular array.
>
> The above is, of course, highly nonrigorous; clearly, the weak point is the definition of "essential" configuration changes. The result, however, seems hardly to be questionable. It is, then clear, that in any situation where the potential energy dominates kinetic energy and entropy ... a system of particles obeying a simple potential will take up a regular lattice structure. (Reproduced from pp. 12–15 of Ref. 24, with permission of the publisher.)

Many find the above argument convincing on first reading; however, it is instructive to consider the following. Assuming our system has a periodic ground state, if we choose a box which would contain many unit cells then, indeed, after minimizing the energy in that box we would expect that "essential" changes would require a lot of energy. But what if the box was much smaller than the expected unit cell? Then we would not be surprised if the configuration changes "essentially" with n, at low cost in energy. Therefore since all we are trying to show is that the unit cell is finite, the argument is, in fact, strictly circular. Indeed, we will exhibit in Sec. 6 toy models which have infinite unit cells (though admittedly our models will not be quite as simple as Anderson's).

Another traditional approach to the crystal problem (which, however, only attempts to understand close packed structures), is based on the mathematical sphere packing problem. This argument is also fallacious, as will be seen in Sec. 3.

The last set of ideas we note in this section is of a different character. They show that, under certain restrictions, there can be no statistical mechanical model of a crystal in low spatial dimensions; more specifically there can be no 1- or 2-dimensional continuum classical model, nor any 1-dimensional alloy model (classical or quantum), which is crystalline at nonzero temperature. For details on continuum models see Refs. 25 and 26, and on alloy models see p. 136 in Ref. 13 and Ref. 27. However, as we discussed in Sec. 1, these considerations, which concern the relative dominance of entropy and energy in the free energy as a function of spatial dimension, are not relevant for the crystal problem.

This brings us up to the recent efforts, of the last decade or so, which are detailed in Secs. 6 and 7, after some necessary preliminaries.

3. Mathematics of the Crystal Problem

In this section we will elaborate on the fundamental mathematical nature of the crystal problem. For indeed the problem is not just of great interest in physics, but is also of fundamental importance in mathematics. This would not be the case if solutions of the optimization problem (minimizing a free energy) were crystalline only for Coulomb interactions, or only for a very special class of interactions. The fact is, from physical considerations (namely the wide variety of "bonds", all of which produce crystals) we expect this to be true for *any* "reasonable" interaction, and this is borne out by many years of experience with models. (Degenerate cases in which the ground state is not essentially unique will be discussed below. Here we just note that in such cases there always seemed to be at least one periodic minimum.) So mathematically we have a general minimization problem, of a function, $(e - Md)$, of many variables (the particle positions and, possibly, internal variables), and we want to understand why the minimum must occur at a periodic configuration of the variables.

We will begin with some comments on a relevant article by Waterhouse[28] entitled "Do symmetric problems have symmetric solutions?". The author considers a number of symmetric problems, such as minimizing the sum of n positive numbers whose product is fixed, and notes that the solutions to such symmetric problems are frequently highly symmetric.

One formulation of his thesis is: **Theorem**. Let f and g be symmetric functions of n real variables, with continuous second derivatives in a neighborhood of the symmetric point $P = (r, \ldots, r)$. On the set where g equals $g(P)$, the function f will have a local maximum or local minimum at P except in degenerate cases.

Two points are in order. First, this argument only tries to show that symmetric points are extrema, and does not attempt to characterize *all* local or global extrema. In particular it is certainly not true that global extrema of f are always symmetric in the generality he considers. Now the problem we are interested in, the crystal problem, consists of showing that a global minimum *must* have a certain symmetry, that is, we need to show that symmetry is forced by, not just consistent with, the extremum process. It is obvious that any close packed configuration, with the right choice of nearest neighbor separation, would yield a *local* minimum of the energy density for the Lennard-Jones interaction. But this is trivial compared with the deep problem of showing that the global minimum must be crystalline (in fact the hexagonal close packed structure; see Ref. 29 however for possible complications due to crystalline growth). Before leaving this line of argument we should mention the beautiful examples of symmetric solutions to symmetric problems discussed by Polya.[30]

The rest of this section will consist of a review of two famous unsolved mathematical extremum problems which will be seen to be intimately connected with the crystal problem.

The first is the "packing problem", in which one has an unlimited number of solid, unit volume spheres in three dimensions and it is desired to find an arrangement of them which would occupy the greatest possible fraction of space. (To be precise, given a nonoverlapping arrangement, A, of the solid unit volume spheres consider an increasing sequence, $S(n)$, of new (hollow) spheres, all centered at one point, where $S(n)$ has radius n, and let $d(A)$ be the lim inf, as n goes to infinity, of the fraction of the

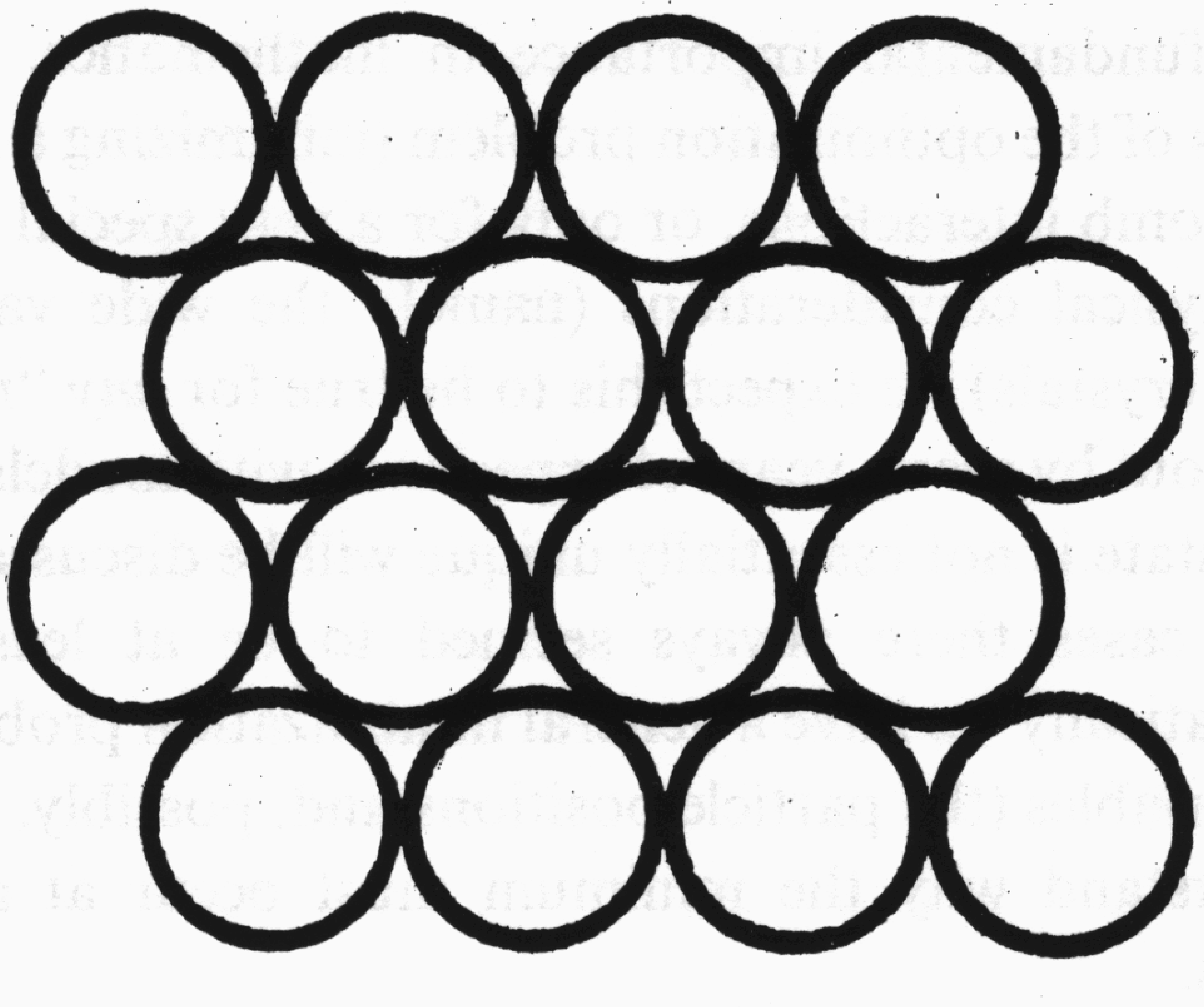


Fig. 4. Planar hexagonally packed structure.

volume of $S(n)$ which is contained in those solid spheres inside $S(n)$. What is then desired is the supremum of $d(A)$ over all possible arrangements A.)

The packing problem has a long history[31] but is still unsolved. For many years, however, it has been believed that the solution is degenerate, and that the highest density is attained among other ways by any of the so-called close packed structures obtained by layering planar hexagonally packed configurations (Fig. 4) together: the most common examples being the face centered cubic and hexagonal close packed structures (see Fig. 5). Since there is a choice of two possible ways of building close packed structures when adding each successive layer, the conjecture is that there are uncountably many distinct ways to achieve the highest density.

There are several ways to connect the packing problem with the crystal problem. If we imagine point particles with only a hard core interaction of radius R, then the crystal problem is to minimize $(e + P)/d$ and this is precisely the packing problem (for any fixed $P > 0$). Note therefore that reference to the sphere packing problem does not solve the crystal problem, for three reasons. First, the packing problem is not solved, so even if the conjectured solution is correct we have no useful understanding of it. Second, this line of argument can only be relevant for close packed solids, so it is not general enough. And the third and most important reason is that in the presumed solution of the packing problem we do not, in fact, find periodicity forced at all, but have a degeneracy which includes nonperiodic configurations.

A more realistic model adds to the hard core a Lennard-Jones type interaction, V, with the hard core radius much smaller than the separation which yields the minimum value, $-m$, of V. In the limit where m/P goes to zero, we recover the previous packing problem, with degenerate conjectured solution. In the limit where m/P goes to infinity we recover our prototype for the crystal problem (in which we minimize the energy per particle of N particles interacting through the Lennard-Jones potential).

One interesting consequence of adding V to the hard core is that (presumably) it removes the degeneracy of the ground state. (It is not hard to prove that, among all the "layered" configurations discussed above, the hexagonal close packed structure

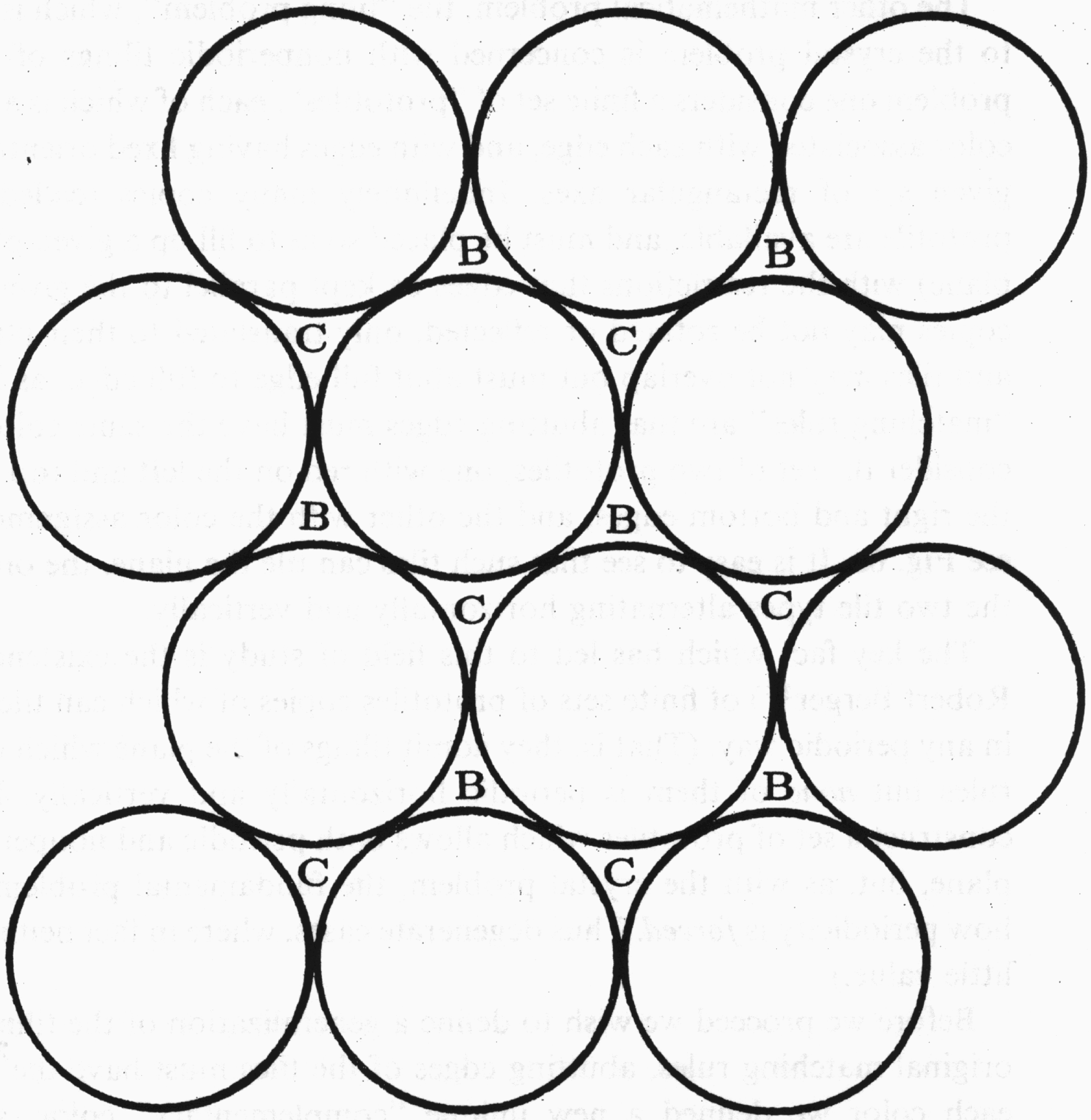


Fig. 5. Close packed structures. If bottom layer (with circles) is called *A*, then over this one can fit tightly either of two types of layers, centered over letters *B* or *C*. The face centered cubic structure corresponds to the sequence *ABCABC*. . ., and the hexagonal close packed structure to *ABABAB* . . . .

gives the unique minimum for the energy per particle.[32]) Thus, the crystal problem leads to a natural generalization of the packing problem, and at the same time removes its (presumed) degeneracy. (The degeneracy could be interpreted as implying that the packing problem requires reformulation.) It also shows that the traditional emphasis on lattice solutions of the packing problem, which correspond to crystals with a unit cell of one particle, is inappropriate: a more natural class is that of periodic configurations.

It is worth noting that the packing problem has been generalized in other ways, notably to spatial dimensions other than three. In one and two dimensions it has unique solutions, (which happen to be periodic), and is unsolved in three and higher dimensions.[31] A different generalization, used in the study of glasses, is to curved 3-dimensional spaces. One part of the idea there is that in an appropriately curved space tetrahedra can be packed together to fill all of space, and thus solve the packing problem in that space.[33,34]

The other mathematical problem, the "tiling problem", which is closely connected to the crystal problem is concerned with nonperiodic tilings of the plane. In this problem one considers a finite set of "prototiles", each of which is a unit square with a color associated with each edge, and with edges having fixed orientations parallel to a given set of rectangular axes. Indefinitely many copies (called "tiles") of each prototile are available, and must be placed so as to fill up a given plane (i.e. "tile" the plane) with the restrictions that edges be kept parallel to the given axes (that is, the copies may not be rotated or reflected, only translated to their places in the plane), and tiles may not overlap but must abut full edge to full edge, as in a tile floor. The "matching rules" are that abutting edges must have the same color. As an example, consider the set of two prototiles, one with red on the left and top edges and blue on the right and bottom edges, and the other with the color assignments interchanged; see Fig. 6a. It is easy to see that such tiles can tile the plane, the only way being with the two tile types alternating horizontally and vertically.

The key fact which has led to this field of study is the existence (first shown by Robert Berger[35]) of finite sets of prototiles copies of which can tile the plane but not in any periodic way. (That is, they admit tilings of the plane which obey the matching rules but *none* of them is periodic horizontally and vertically. It is very easy to construct a set of prototiles which allows both periodic and nonperiodic tilings of the plane, but, as with the crystal problem, the fundamental problem is to understand how periodicity is *forced*. Thus degenerate cases, where in fact neither is forced, are of little value.)

Before we proceed we wish to define a generalization of the tiling problem. In the original matching rules, abutting edges of the tiles must have the same color. If for each color we defined a new unique "complementary" color, and a new set of prototiles were made with complementary colors replacing the originals on the right and top edges, and if the matching rules were redefined by requiring abutting edges to have complementary colors (see Fig. 6b), we would clearly get an example isomorphic to the original: there would be a natural one to one correspondence between the tilings of the plane by the two sets of tiles. It is now easy to get a further generalization of the tiling problem by replacing each color associated with an edge by a unique sequence of bumps and dents on the edge, bumps and dents placed so that for complementary edges bumps fit into dents; see Fig. 6c. In this way we replace colored tiles with tiles which are only "essentially" unit squares, and the new matching rules require the tiles to fit together as in a jigsaw puzzle. Notice that in placing bumps and dents we should avoid corners as this could introduce matching rule restrictions on tiles which are only diagonally touching, not abutting. Such a restriction changes the rules in an essential way, but is not necessarily bad. In fact we will allow this generalization, referring to such new restrictions as "corner conditions". The last type of generalization we will introduce is to allow copies of prototiles to be rotated and/or reflected, as well as translated, in tiling the plane. To summarize, besides the original tiling problem we now have several generalizations where we use complementary

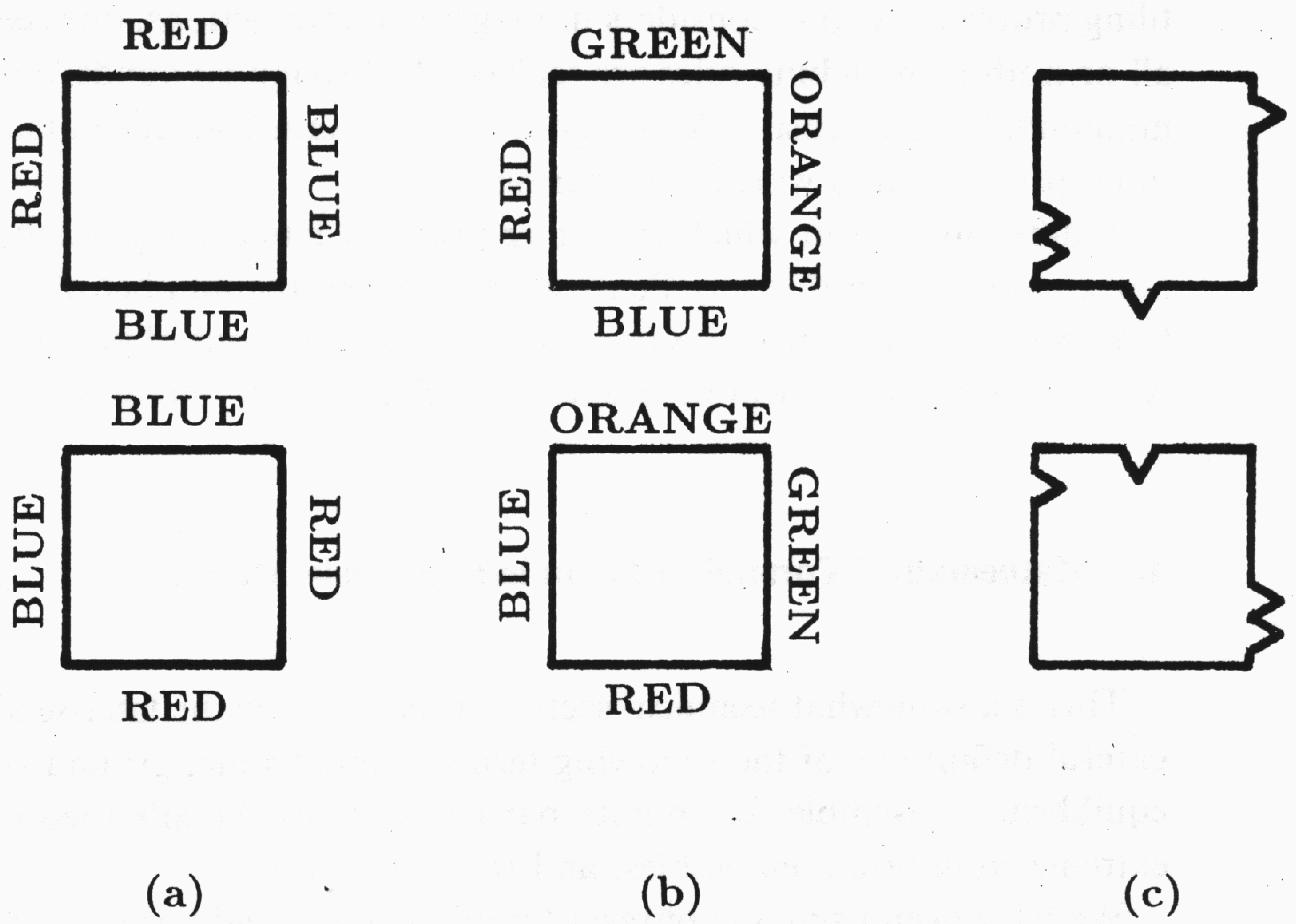


Fig. 6. Different versions of a simple tiling example.

colors, and/or bumps and dents, and/or corner conditions, and possibly allow rotations and/or reflections of the tiles.

Ever since Berger's example noted above, a serious effort has been made to understand what it is, about a set of prototiles, which does or does not force nonperiodicity. This is still unknown, and the construction of examples is still somewhat of an art. (The smallest set we know of which forces nonperiodicity and follows the original rules is due to Ammann[36] and contains sixteen prototiles. If reflections, rotations and corner conditions are allowed the smallest set we know of contains six prototiles and is due to Robinson[37]. Both sets are described in Sec. 6.) The standard reference for the tiling problem is the recent important work of Grünbaum and Shephard,[36] especially Chaps. 10 and 11.

The connection between the tiling problem and the crystal problem is the following. Consider a "tiling example", that is, a set of N prototiles, and define a 2-dimensional alloy model on the square lattice, with any one of N possible species (one for each of the N prototiles of the tiling example) occupying each lattice site. Define a nearest neighbor interaction between a pair of species to be -1 if the corresponding prototiles match and $+1$ if they do not match. (The interaction is also next-nearest neighbor if corner conditions are allowed.) All chemical potentials are taken to have value 0. It will be important in Sec. 6 that, if any of the above prototile sets which force nonperiodicity are used, the corresponding statistical mechanical model has a unique ground state which is not, however, periodic but only "quasiperiodic".

The above construction suggests a very natural generalization of the mathematical tiling problem. As one considers more general interactions, one sees that the original all-or-nothing matching rules are replaced by "weighted bonds" and the condition of minimum energy density. Although it is not certain that this in fact would enrich the tiling problem, it is worth considering.

A different way in which the tiling problem has been generalized is by allowing nonsquare tiles. In this way Penrose has reduced the number of prototiles needed to force nonperiodicity from six (if rotations and reflections of prototiles and allowed) to two. These examples will be discussed in Sec. 6 with reference to quasicrystals.

4. Mathematical Formalism for Infinite Particle Models

This is a somewhat technical section, necessary for the later sections, and contains careful definitions of the following terms; ground state, ground state configuration, equilibrium ensemble for infinite particle systems, Sinai's theorem, faults, mixing, extreme equilibrium ensembles, and fraction space.

We have been using the phrases "ground state" and "ground state configuration" quite a bit, and it is time to give them precise meanings. By "configuration" we mean a single assignment or array of positions (and internal states if appropriate) for a finite or infinite collection of particles. Mathematically, the word "state" means probability distribution, or ensemble; by "ground state" we refer to an ensemble of configurations which corresponds to zero temperature in the sense that it is the limit of nonzero temperature ensembles as temperature approaches zero, with other variables associated with the ensembles, such as pressure for pressure ensembles, kept fixed.

For a system of finitely many particles, the above is simple: a ground state is just a probability distribution supported by those configurations, constrained to some large box, which minimize $E - PV$ for a pressure ensemble, or $E + MN$ for a grand canonical ensemble, of a simple system; here E is the total energy, N is the number of particles, and V is the volume. For finite systems then, the above configurations in the support of ground states are called "ground state configurations".

The only infinite particle systems we will consider are alloy models, and for these we will use the DLR formalism (named for Dobrushin,[38] Lanford and Ruelle[39]), which is a grand canonical formalism. Thinking of the space of configurations as the Cartesian product of the finite one particle spaces, S, at each site, it is compact and metrizable in the product topology. Before we can discuss equilibrium ensembles (which are probability distributions on the set of configurations), we need to restrict the types of interactions which will be allowed.

Let Ω be the space of configurations on $\mathbf{Z}^\nu$ (which we will often think of as functions from $\mathbf{Z}^\nu$ to the one particle space S), let $\mathbf{F}$ be the set of all finite subsets of $\mathbf{Z}^\nu$ and, for each F in $\mathbf{F}$, let Ω_F be the set of all configurations on F, with $\Omega_\emptyset$ defined as a point. Furthermore, if $\mathbf{Z}^\nu \supseteq G \supseteq F$ and $g \in \Omega_G$, we denote by $g|_F$ the restriction of g to F.

Interactions V are real valued, translation invariant functions on the disjoint union $\dot{\bigcup}_{F\in\mathbf{F}}\Omega_F$ for which $V(\Omega_\emptyset) = 0$. (Think of $V(f)$ as the many-body interaction associated with the finite configuration f.) The interaction V is of finite range $<R$ if $V(f) = 0$ whenever $f \in \Omega_F$ and the diameter of F is at least R. We define the norm $\|\cdot\|$ on the space of all interactions by

$$\|V\| = \sum_{F\in\mathbf{F},F\ni 0} \sum_{f\in\Omega_F} |V(f)|$$

and we define the space I to be the weighted l_1-space consisting of those interactions with finite norm. It is convenient for later purposes to give a slightly different description of I. Consider the set of all equivalence classes, modulo translations of $\mathbf{Z}^\nu$, of elements of $\mathbf{F}$ containing 0 — note that the class containing F has *card*(F) members, where *card* stands for cardinality — and define $\mathbf{F}_0$ as any set (hereafter fixed) consisting of precisely one member from each equivalence class. Finally let K be the set of all pairs, (F, f), where $F \in \mathbf{F}_0$ and $f \in \Omega_F$. (Think of K as a list of all possible ways of "coloring" finite subsets of $\mathbf{Z}^\nu$.) Then

$$\|V\| = \sum_{(F,f)\in K} |V(f)|\, card(F).$$

Our next goal is to define equilibrium (or Gibbs) ensembles, for which we follow Ref. 40. Assume the temperature $T > 0$ and interaction $V \in I$ are fixed. For any $F \in \mathbf{F}$ and $f \in \Omega_F$ we define

$$U_V(f) = \sum_{H\subseteq F} V(f|_H).$$

If also $g \in \Omega_{F^c}$, *where* F^c is the complement $\mathbf{Z}^\nu \backslash F$, let

$$W_V(f, g) = \sum_{X\subseteq\mathbf{F},X\cap F\neq\emptyset,X\cap F^c\neq\emptyset} V([f \vee g]|_X),$$

where $f \vee g \in \Omega$ is the function whose restriction to F is f and to F^c is g. Furthermore, define

$$\Xi_{V,T;F}(g) = \sum_{h\in\Omega_F} \exp - [U_V(h) + W_V(h, g)]/T$$

and

$$\mu_{V,T;F}(f, g) = \frac{\exp - [U_V(f) + W_V(f, g)]/T}{\Xi_{V,T;F}(g)}.$$

(Note that, for each "boundary condition" g, $\mu_{V,T;F}(\cdot, g)$ defines a Gibbsian probability distribution on Ω_F.) If k is a continuous function on the compact space Ω and $f \in \Omega$, we define the (continuous) function $\Upsilon_{V,T;F}k$ on Ω by

$$\Upsilon_{V,T;F}k(f) = \sum_{h \in \Omega_F} k(h \vee f|_{F^c})\mu_{V,T;F}(h, f|_{F^c}).$$

Finally, we say the probability distribution μ on Ω is an "equilibrium ensemble (corresponding to the temperature T and interaction V)" if it satisfies the DLR equations, namely

$$\int_\Omega k(f)d\mu(f) = \int_\Omega \Upsilon_{V,T;F}k(f)d\mu(f)$$

for all $F \in \mathbf{F}$ and continuous functions k on Ω. (See Ref. 40 for a clear justification of this as a grand canonical formalism of infinite particle systems.)

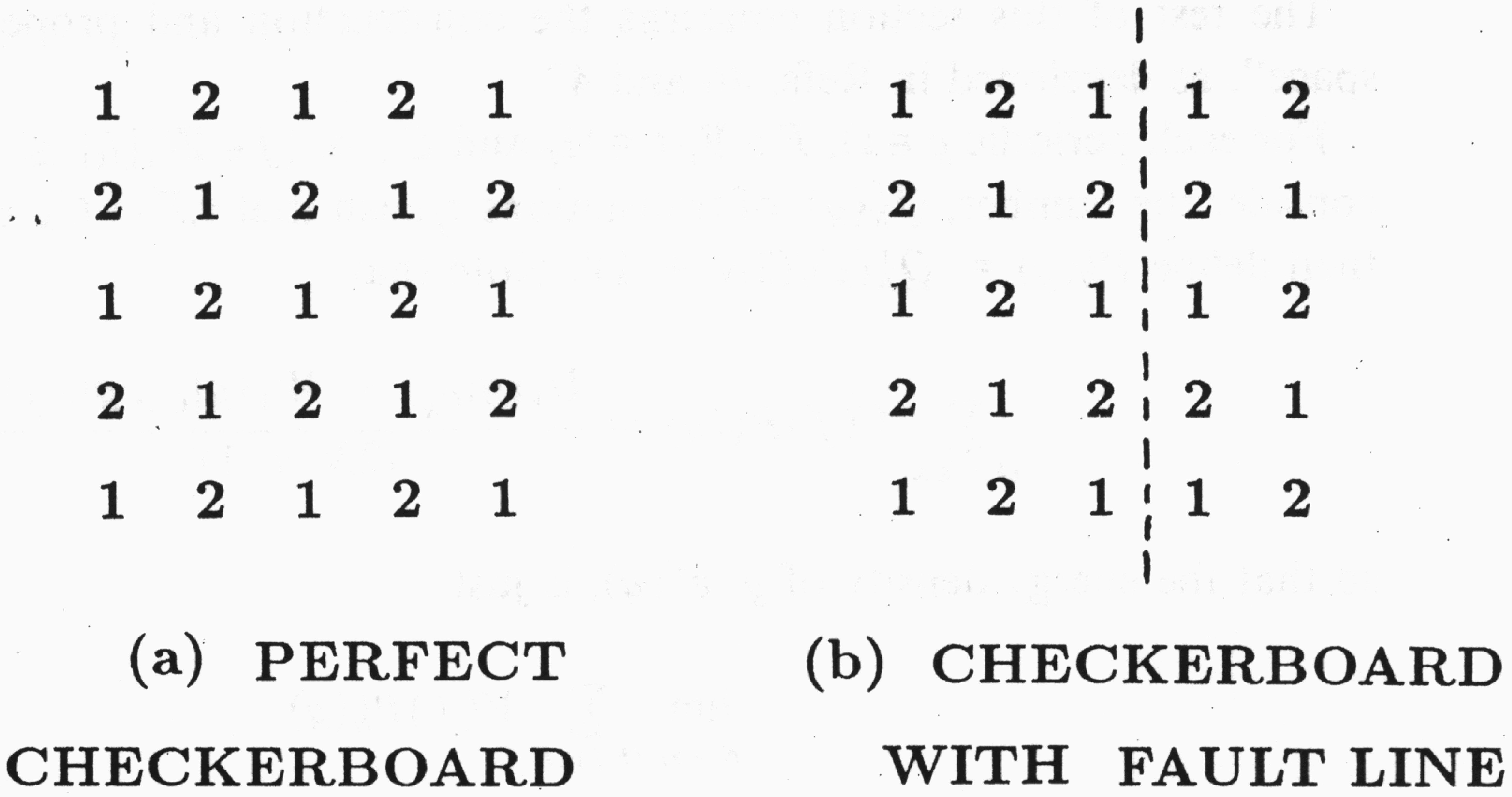
We are primarily interested in ground states, that is, limits (technically, weak-* limits) of these ensembles as temperature T approaches zero. At least for finite range interactions there are DLR equations for such limits,[41] but we will not need them here. Instead we will use "ground state configurations" defined as followed. The configuration $f \in \Omega$ is a ground state configuration for the interaction V if for every $F \in \mathbf{F}$

$$\inf_{g \in \Omega}\{U_V(g|_F) + W_V(g|_F, f|_{F^c})\} = U_V(f|_F) + W_V(f|_F, f|_{F^c}).$$

Roughly this equation is a requirement of minimal energy density; it is important to note that it requires that the energy density be minimized not just locally, but absolutely. Now from the definition a configuration is a ground state configuration if and only if in some precise sense it is optimal in comparison with all possible configurations. There is however a very useful theorem of Sinai's — p. 36 in Ref. 42 — which shows that a *periodic* configuration f is a ground state configuration if and only if it is optimal, in the same sense, with respect to all possible *periodic* configurations; to be precise, if for every $F \in \mathbf{F}$.

$$\inf_{g \in \Omega, g \text{ periodic}} \{U_V(g|_F) + W_V(g|_F, f|_{F^c})\} = U_V(f|_F) + W_V(f|_F, f|_{F^c}).$$

The importance of the notion of ground state configuration is that, for given interaction $V \in I$, the set of all ground state configurations is compact and contains the support of every ground state.[43] By the way, the "containment" may be proper. For example, for the statistical mechanical model based on the tiling example of Fig. 6, the only ground states are of the form $\alpha\delta_1 + (1 - \alpha)\delta_2$, where δ_1 is a point mass on a perfect checkerboard configuration (see Fig. 7a), δ_2 is the point mass on the same configuration translated one space, and $0 \leq \alpha \leq 1$; however there are ground state



1 2 1 2 1
2 1 2 1 2
1 2 1 2 1
2 1 2 1 2
1 2 1 2 1

(a) PERFECT CHECKERBOARD

1 2 1 | 1 2
2 1 2 | 2 1
1 2 1 | 1 2
2 1 2 | 2 1
1 2 1 | 1 2

(b) CHECKERBOARD WITH FAULT LINE

Fig. 7. Patterns of two symbols.

configurations with "faults" as in Fig. 7b, which have nothing to do with ground states, at least in this two dimensional model — see Ref. 44 for differences in the three dimensional version of the model. Anyhow, this model illustrates how one can hope to understand ground states through ground state configurations.

There is one theorem about equilibrium ensembles that we will need in Sec. 5. It concerns the notion of mixing (or clustering) of probability distributions defined on spaces acted on by some abelian (translation) group, which we will now define. For clarity we will restrict attention to the main example of interest, where the probability distribution, μ, is defined on the compact configuration space, Ω, of an alloy model. For any nonempty subset $F \in \mathbf{F}$ and $f \in \Omega_F$, consider the "cylinder set" $\{g \in \Omega | g|_F = f\}$ and let χ_f denote the characteristic function of this set, that is the function on Ω which is 1 on the set and 0 off the set. Then if translation by $j \in \mathbf{Z}^\nu$ of the configuration $x \in \Omega$ is denoted by $\tau_j(x)$, we say the translation invariant distribution μ is mixing or clustering (technically, n-fold mixing for all n) if for any n such characteristic functions, $\chi_{f_1}, \ldots, \chi_{f_n}$

$$\lim \int_\Omega \chi_{f_1}(\tau_{j_1}x) \ldots \chi_{f_n}(\tau_{j_n}(x)) d\mu(x) = \int_\Omega \chi_{f_1}(x) d\mu(x) \ldots \int_\Omega \chi_{f_n}(x) d\mu(x),$$

where in the limit all pairs of j's get arbitrarily far apart. Intuitively, this means that for such an ensemble events which are associated with distantly separated regions of space are approximately independent.

We need one further notion to describe the theorem to which we alluded. If $G_T(V)$ denotes the set of all equilibrium ensembles for the interaction V at temperature T, $\mu \in G_T(V)$ is said to be extremal if it cannot be expressed in the form $\mu = \alpha\mu_1 + (1 - \alpha)\mu_2$ for any $0 < \alpha < 1$ and μ_1, μ_2 in $G_T(V)$. The theorem then states that any extremal equilibrium ensemble is mixing.[39,45]

The rest of this section concerns the construction and properties of "fraction space", as developed in Refs. 46 and 47.

For each periodic $g \in \Omega$, $F \in \mathbf{F}$, $f \in \Omega_F$ and $C_N \equiv \{j \in \mathbf{Z}^\nu \,|\, |j_k| \leq N, k = 1, \ldots, \nu\}$, consider the number, $Q_N^f(g)$, of translations τ_j such that $\tau_j F \cap C_N \neq \emptyset$ and $f = \tau_j g|_F$; then define $P_N^f(g) = Q_N^f(g)/(2N + 1)^\nu$. Note that

$$\sum_{(F,f) \in K} V(f) P_N^f(g) = \frac{U_V(g|_{C_N}) + W_V(g|_{C_N}, g|_{C_N{}^c})}{(2N + 1)^\nu}$$

so that the energy density of g, $e^V(g)$, is just

$$\lim_{N \to \infty} \sum_{(F,f) \in K} V(f) P_N^f(g).$$

If we consider the function, $P(g)$, in $l_\infty(K)$ which at each $(F, f) \in K$ has the value

$$\lim_{N \to \infty} P_N^f(g)/(2N + 1)^\nu$$

then $\|P(g)\|_\infty \leq 1$ and $e^V(g) = \langle V, P(g) \rangle$, where $\langle \cdot, \cdot \rangle$ is the canonical duality between the weighted l_1-space, I, and its dual, $l_\infty(K)$. Finally, we define fraction space, B, as

$$B \equiv \textit{weak-}* \textit{ closure } \{P(g) \in l_\infty(K) | g \in \Omega, g \textit{ periodic}\}.$$

The function $P(g)$ is just the list of the frequencies with which each "finite colored pattern", that is, each $f \in \Omega_F$ for any $F \in \mathbf{F}$, *appears* (when averaged over translations) in the periodic configuration g; it contains precisely that information about g needed to compute its energy density. Of course "most" patterns do not appear at all for any given g, so $P(g) = 0$ at most points of K; on the other hand, since g is periodic any pattern which appears at all appears with nonzero frequency. For example for a two-dimensional alloy model with two species, "red" and "black", the pattern f, consisting of black on one site and red on the neighboring site to the right, has frequency 1/2 in a checkerboard configuration g.

It is easy to see that for "most" nonperiodic configurations g there is no well defined $P(g) \in B$, and that many points in B do not correspond to any configuration g, neither periodic nor nonperiodic. Also, one can check that B is a convex, weak-$*$ compact subset of the unit ball of $l_\infty(K)$.

Now a key fact here is that for any ground state configuration f of the interaction $V \in I$, the energy density $e^V(f)$ exists (this is easy) and

$$e^V(f) = \inf\{e^V(g) | g \in \Omega, g \textit{ periodic}\}.$$

In other words, $e^V(f)$ is the infimum of the values $\langle V, P \rangle$ as P varies throughout B, which, as we know from elementary linear programming, is attained when a hyperplane whose normal is V is translated in a parallel fashion to an edge of the convex set B, becoming a supporting hyperplane to B. Generalizing the well known situation in finite dimensions, it can be shown that for generic interactions $V \in I$ (that is, for a set containing a countable intersection of dense open sets of V's) the supporting hyperplane touches B at a unique point, P_V. For such V it happens that *every* ground state configuration f has the *same* well defined frequency function $P(f)$, with $P(f) = P_V$ and so $e^V(f) = \langle V, P(f) \rangle$. A more technical way of describing this is that each of a generic set of V's has a unique translation invariant ground state, and furthermore when this ground state is restricted to its support in Ω — or more generally to the set of ground state configurations — it is uniquely ergodic under translations. (For references to the relevant ergodic theory see Refs. 48 and 49.)

5. Long Range Order

Our basic problem is to understand why matter tends to be crystalline at low temperature. This section is devoted to an exploration of some possible meanings of "crystalline".

One's first mental picture of a crystal is, for most people, that of some perfect periodic point set such as Fig. 1. Then to take into account the effects of nonzero temperature it is natural to add to the picture some random local defects, "local" so as to preserve "long range order". Now our mathematical model consists of a statistical ensemble, which is just a probability distribution on the set of all possible many particle configurations: it distinguishes which distributions are "more likely" from those which are "less likely". Our mental picture of a single perfect lattice corresponds to a probability distribution concentrated at a single point; or, if one insists on translation invariant distributions, on the set of translates of this one point (*i.e.* the orbit under translations of the point in the set of configurations.) So one expects the zero temperature distribution to be some sort of delta function. And the nonzero temperature distribution should be a smeared out version of this delta function. In what way is such a distribution distinguishable as a crystal? How does one describe the "order" that should be in the (smeared) delta function?

For historical reasons we expect to use the mathematics of the Euclidean group; we expect to see this group make itself felt in the crystalline phase. At present this occurs only in a minor way. In terms of alloy models (on which we concentrate for the rest of this section), we try to compute the n-point function $r(s_1, \ldots, s_n)$ and show that (at appropriate temperature and chemical potentials) it peaks precisely when each species occupies sites "periodically", that is, corresponding to some subgroup of the translation group. So the group is really only entering as a shorthand to describe certain configurations. But in what way are these configurations "ordered"?

To handle this we use the notion of conditional probability as follows. When we say an ensemble exhibits "long range order" we mean, intuitively, that given knowledge of the structure of configurations in some local region this has import on the structure of configurations very far away. The "knowledge" and "import" are of course probabilistic. This is made quantitative in the notion of "clustering", or its mathematical equivalent, "mixing", of an ensemble which was defined in Sec. 4. Note that an ensemble which is concentrated at one configuration is mixing, no matter how disorderly the configuration. However if one restricts attention to translation invariant ensembles, it is important to note that the average over translations of an ensemble concentrated at a "random" configuration is mixing (as one sees by the ergodic theorem), while there are only a finite number of distinct translations of a crystalline configuration and the average over translations of an ensemble concentrated at a crystalline configuration is therefore easily seen to be nonmixing. So the order in a configuration can be revealed by averaging over its orbit under translations.

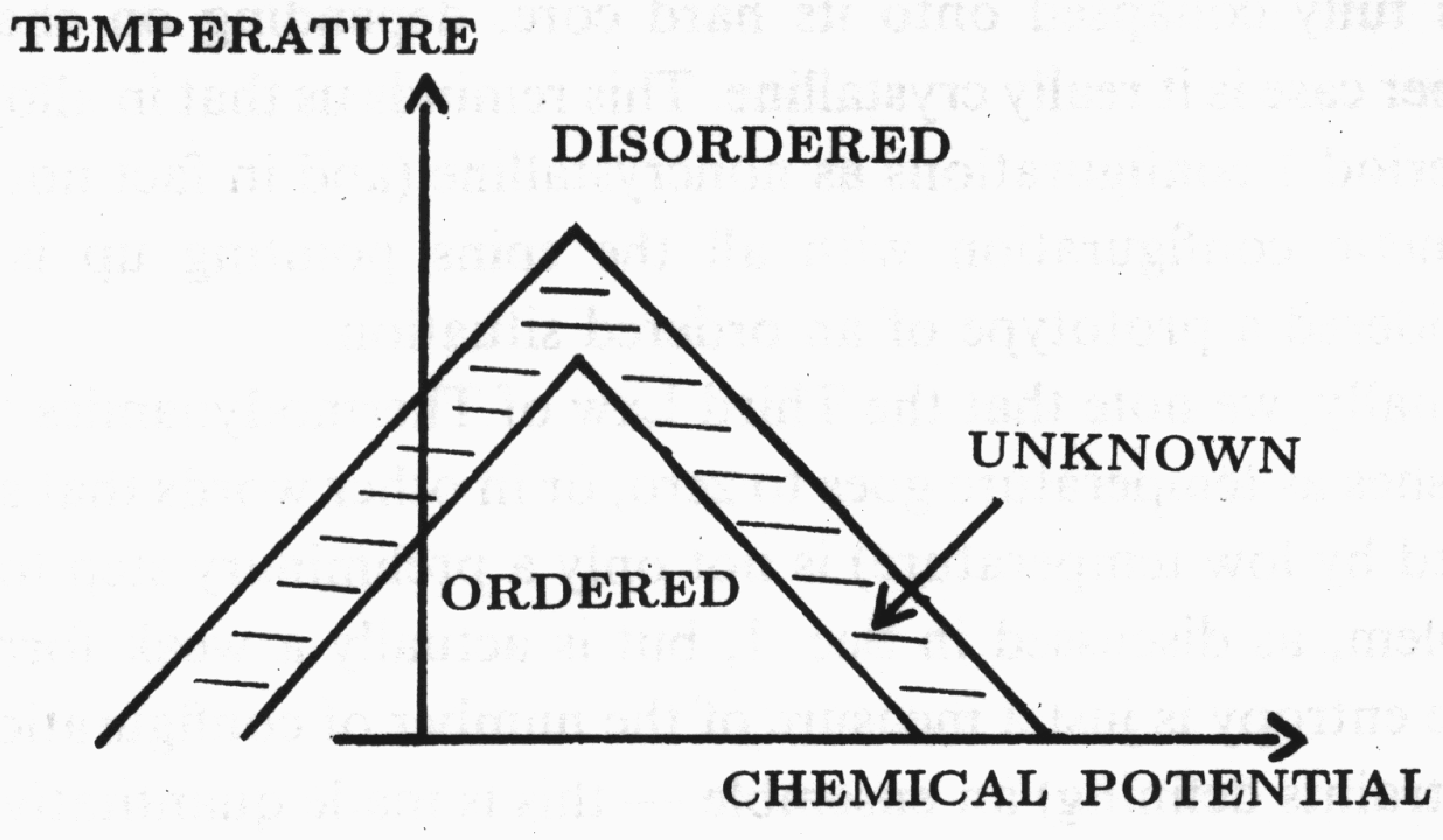
One traditional way to realize our intuitive concept of order is to prove that there is an "order parameter" associated with low temperature matter, that is, a quantity which is nonzero in the low temperature (ordered) phase but which vanishes at high temperature, thus having incompatible analytic representations in the two regimes. (By incompatible we mean the two functions cannot be analytically continued to one another but must be separated by singularities, presumably phase transition lines. In particular there must not be a critical point around which one could move analytically from the ordered to the disordered phase; see p. 122 in Ref. 50, p. 76 in Ref. 51 and Ref. 52.) It is useful to consider as a prototype the 2-dimensional one component lattice gas model, with isotropic repulsive nearest neighbor interaction and chemical potential M; see Ref. 53. The phase diagram appears in Fig. 8a. (If the interaction were instead a nearest neighbor exclusion and next nearest neighbor repulsion or attraction, the phase diagram would look like Fig. 8b.) In the disordered phase there is only one equilibrium state (which is therefore extreme equilibrium and translation invariant), and in the ordered phase there are precisely two extreme equilibrium states, each a translate of the other, and mixtures of them.

One way to distinguish the two phases is through the sublattice density

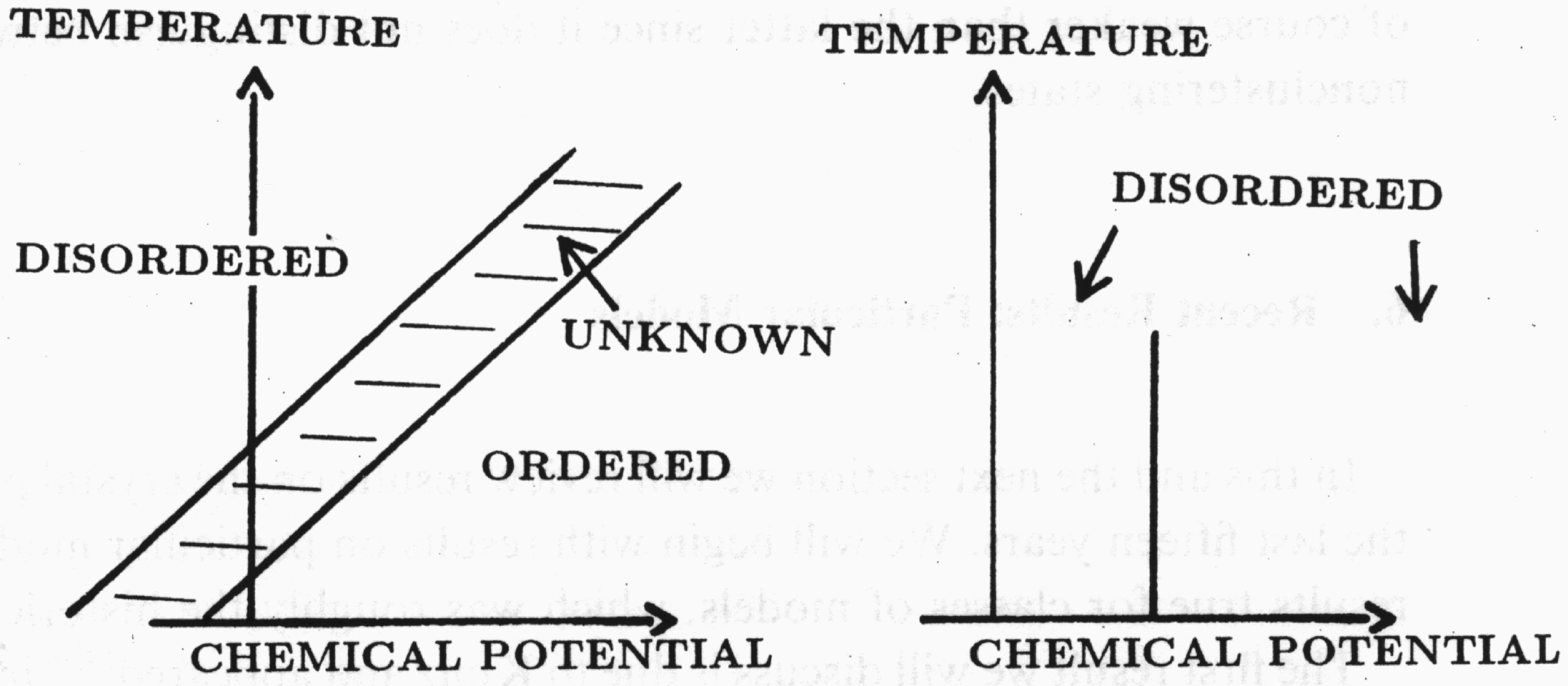
$$\lim_{N\to\infty} \sum_{|m|,|n|\le N} [s_{(2m,2n)} + s_{(2m+1,2n+1)} - s_{(2m,2n+1)} - s_{(2m+1,2n)}]/(2N+1)^2$$

where $s_{(i,j)}$ is 0 (resp. 1) if the site with Cartesian coordinates (i, j) is empty (resp. occupied). In the disordered phase it has value zero (this follows from translation invariance) while in either of the extreme states of the ordered phase it varies (smoothly) with T and M, and thus it is represented by incompatible analytic functions in the two phases.

A different way to distinguish the two phases is through the translation invariant



(a) NEAREST NEIGHBOR REPULSION



(b) EXTENDED HARD CORE (c) NEAREST NEIGHBOR ATTRACTION

Fig. 8. Phase diagrams of simple alloy models.

equilibrium states (see pp. 16–17 in Ref. 4). In the disordered phase there is only one equilibrium state so it clusters (see Sec. 4), while in the ordered phase it is a mixture of the two extreme equilibrium states and does not cluster. Thus the two phases are distinguished by whether or not the (unique) translation invariant equilibrium state clusters. (As we shall see in Sec. 7, it is reasonable to restrict attention to models which have unique translation invariant equilibrium states.)

With regard to this last method we note that there can be some form of order in the presence of clustering, for example at a critical point, but not crystalline order. For this reason we see that the 2-dimensional one component lattice gas model with isotropic nearest neighbor attraction and chemical potential M, which is essentially the 2-dimensional nearest neighbor Ising ferromagnet in external field, is not a reasonable model of crystalline order since the equilibrium state clusters except in a mixed state at one special value of the chemical potential. The phase diagram is Fig. 8c. As a lattice gas model what is happening is that the material has either zero density or is fully collapsed onto its hard core, depending on chemical potential, and in neither case is it really crystalline. This reminds us that in alloy models one must think of period 1 configurations as noncrystalline (and in fact not ordered) even though a magnetic configuration with all the spins pointing up is often, but incorrectly, considered a prototype of an ordered situation.

Finally, we note that the Third Law of Thermodynamics (that is, that the entropy vanishes as temperature goes to zero, or in other words that some measure of order is forced by low temperature) is not only a preliminary step for motivating the crystal problem, as discussed in Sec. 1, but is actually a weak form of the same problem. Since entropy is just a measure of the number of configurations compatible with (the constraints defining) an ensemble — this is made quantitative in an important paper of Aizenman and Lieb[54] — it is intuitively reasonable, from our discussion above on mixing, that "low entropy" and "crystalline order" are related concepts; the former is of course weaker than the latter since it does not distinguish between clustering and nonclustering states.

6. Recent Results: Particular Models

In this and the next section we will review results on the crystal problem obtained in the last fifteen years. We will begin with results on particular models and advance to results true for classes of models, which was roughly the historical route.

The first result we will discuss is due to Kunz and appeared[55,56] in 1974. At that time the only relevant interacting models whose ground states were understood were certain alloy models, for example the lattice gas with one species and nearest neighbor repulsion as noted in Sec. 5, and 1-dimensional continuum models with very short range (trivial) interaction (that is, effectively just nearest neighbor interaction). (As always, we only consider translation invariant interactions.) The model Kunz considered is known as the classical, one component, 1-dimensional jellium model. It consists of N point particles each of charge $q > 0$ in an interval of length L, together with a neutralizing background charge density $\rho = -Nq/L$. Both rigid wall and periodic boundary conditions are considered. It is shown that at all temperatures the system is crystalline in two senses: first there is no clustering, and second the 2-point correlation function, $r(x_1, x_2)$, has a local maximum when x_2 has the value $x_1 + kL/N$, k any integer — both results referring to the unique translation invariant state. (Note that the usual high temperature fluid phase is missing, presumably due to the artificially long range of the force.) Although this model does seem to behave in some sense like a crystal at $T > 0$, it does not really tell us much about the crystal problem. The difficulty can be seen more clearly in the generalized model where more than one component is allowed, each with some positive integer charge. Very similar results are obtained for this model[57] except now the ground state is degenerate, supported by all configurations in which a particle of charge q is centered in an interval of length

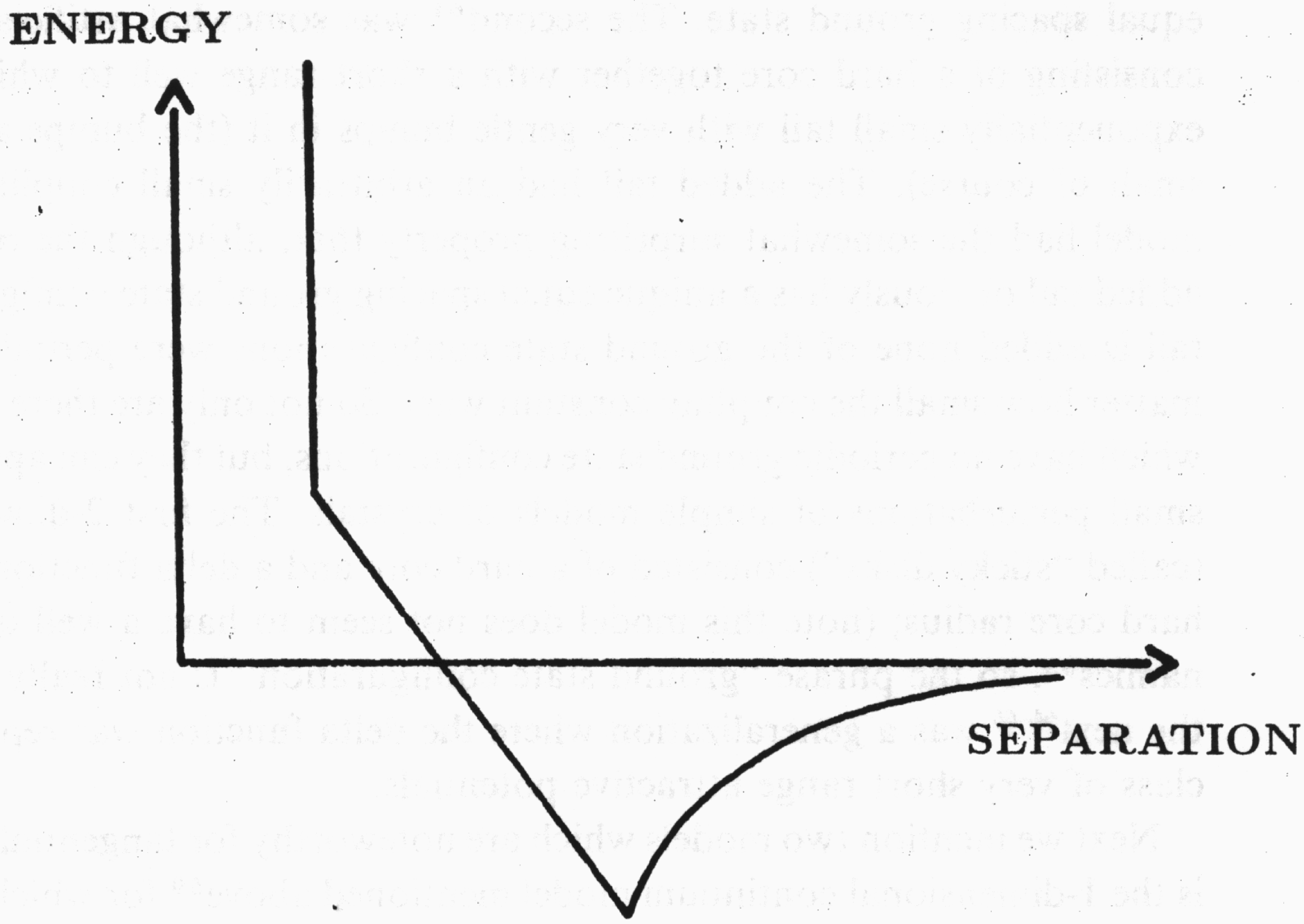


Fig. 9. Ventevogel's example.

$qL/(\sum_j q_j n_j)$ which is otherwise free of particles, where n_j denotes the number of particles of charge q_j. In other words the jellium model does not really force periodicity, only local charge neutrality, and this accidentally leads to periodicity when there is only one component. Thus we will not consider such long range models further for the crystal problem.

The next result of interest was an example by Ventevogel[58] of a 1-dimensional continuum model, with a simple two-body interaction, for which the ground state configurations are not equally spaced. The potential (Fig. 9) is:

$$V(x) = +\infty, \quad |x| < 4/9$$

$$V(x) = 2 - 3|x|, \quad 4/9 \le |x| < 1$$

$$V(x) = -|x|^{-2}, \quad |x| \ge 1.$$

The ground state configurations are shown, by a clever method (the "Ventevogel shift"), to not be equally spaced — a unit cell of two particles has lower energy density — but the actual minimum is not determined. (A similar model, based on this one but for which the unit cell of two particles is shown to produce the minimum energy density, appeared in Ref. 59.)

Four more particular continuum models for which the ground state configurations were determined were the following two 1-dimensional models and two 2-dimensional models. The first 1-dimensional model[60] was the Lennard-Jones model, which has an equal spacing ground state. The second[61] was somewhat artificial, the interaction consisting of a hard core together with a short range well to which was added an exponentially small tail with very gentle bumps in it (the bumps also exponentially small of course). The added tail had an arbitrarily small coupling constant. This model had the somewhat surprising property that, although the model without the added tail obviously has a unique equal spacing ground state configuration, when the tail is added none of the ground state configurations were periodic any longer (no matter how small the coupling constant was). So not only are there (artificial) models which have no periodic ground state configurations, but they can appear as arbitrarily small perturbations of simple models of crystals. The first 2-dimensional model[62] (called "sticky disks") consisted of a hard core and a delta function attraction at the hard core radius; (note this model does not seem to have a well defined thermodynamics[63], so the phrase "ground state configuration" is not really appropriate) and the next[64–66] was a generalization where the delta function was replaced by any of a class of very short range attractive potentials.

Next we mention two models which are noteworthy for tangential reasons. The first is the 1-dimensional continuum model mentioned above[59] for which the ground state configurations are known to have a unit cell of two particles. This model was solved at zero temperature for all values of the pressure and proven to undergo a structural phase transition at a critical value of the pressure. The second is a lattice model used by Lieb and Kennedy[67] to help understand the role of electrons in crystal formation.

What we learn from all the above particular models is roughly that the crystal problem is difficult! With hard work one can prove that some particular, very simple interactions in one and two dimensions have crystalline ground states. However even relatively simple interactions can produce nontrivial unit cells, and artificial interactions can produce infinite unit cells ("infinite unit cell" just being another way of saying nonperiodic configuration) which of course puts some constraints on any solution of the crystal problem.

Perhaps a few words should be devoted to the lack of any 3-dimensional continuum models in the above list. The 2-dimensional models are models of a simple van der Waals solid, and of course lead to a close packed configuraton, namely the triangular lattice: see Fig. 4. Their solution uses the solution of the 2-dimensional sphere packing problem as a starting point. Any attempt to model a 3-dimensional van der Waals solid would thus be severely hampered by the lack of sufficient understanding of the corresponding packing problem, as discussed in Sec. 3: "understanding" because just assuming the solution is not nearly sufficient.

There is one more particular model worth noting.[46] It is a two-dimensional alloy model with nearest neighbor interaction. Its astonishing feature is that it has a nondegenerate ground state which is not crystalline: it is quasiperiodic in the sense used in the theory of quasicrystals. (In the original paper on the model,[46] the word quasiperiodic is not used because the paper preceded the discovery of quasicrystals. The notion of quasiperiodic is currently used in several senses as it is not yet understood what would be the most useful definition. One possibility is the following: a configuration f is quasiperiodic if, given any $\varepsilon > 0$ there is a periodic configuration,

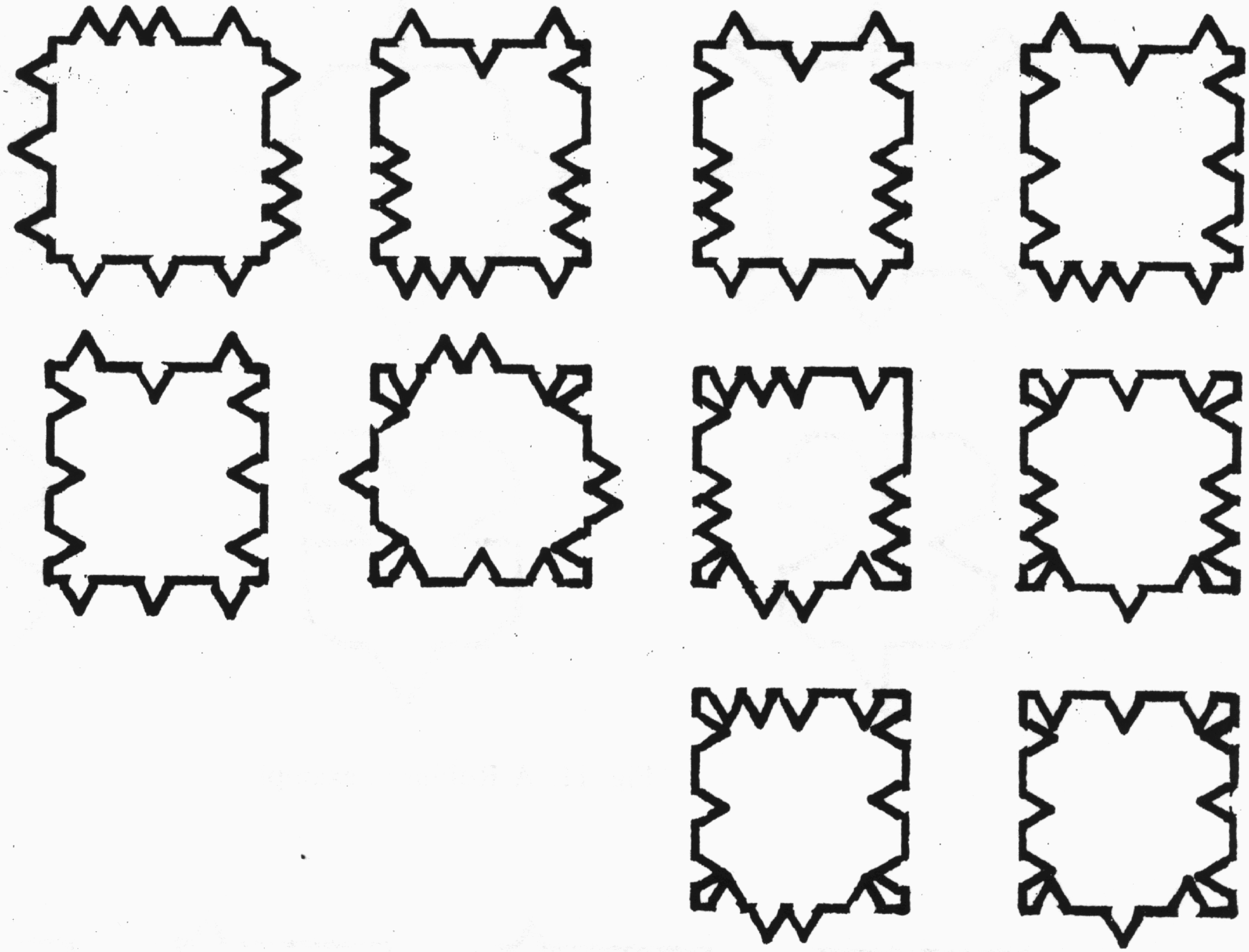


Fig. 10. A Robinson example.

g_ε, which agrees with f off a set of sites of density less than ε, with the periods of g_ε blowing up as $\varepsilon \to 0$.) The existence of a model that has no periodic ground state is not by itself so surprising since, after all, we noted a 1-dimensional model with this property above. There are however several new features here. The first is that the interaction (which we will describe in detail below) is not particularly artificial: it is just a nearest neighbor alloy model with a finite number of simple interaction constants, just 0's and 1's. And the second feature is that any model which is a small perturbation of this model must, if it is not itself quasiperiodic, have periods which blow up as the perturbation vanishes — so something very strange is going on in a whole neighborhood of such an example. (There will be two other features noted below, concerned with the response of the models to temperature, and their relevance for quasicrystals.)

We will now describe the model in detail. (In fact we will describe not just one model but a family of models, all closely related.) Being a 2-dimensional alloy model, all that need be specified is the number of species and the interaction constants. These are fixed by a choice of a set of prototiles of a nonperiodic tiling example (not allowing rotations or reflections), as discussed in Sec. 3. Three particular tiling examples are worth noting. The first[37] has 56 prototiles, which can all be obtained by rotation and reflection of a subset of 10 of them (Fig. 10). The second[37] has 32 prototiles with corner conditions, which can all be obtained by rotation and reflection from a subset of 6 of them (Fig. 11). And the third[36] (Fig. 12) has 16 prototiles.

Although it would seem that the model using the last tiling example would yield a

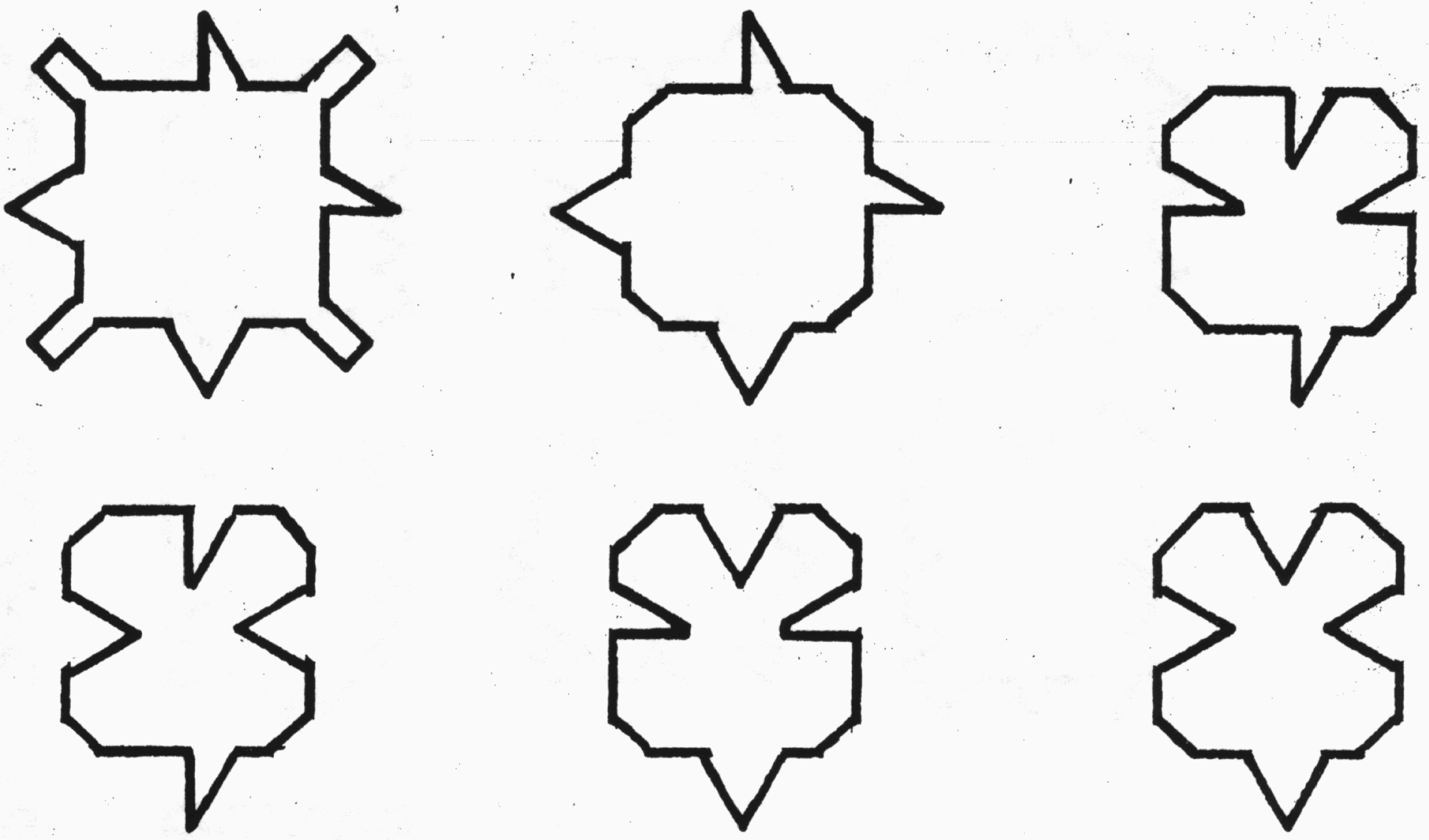


Fig. 11. A Robinson example.

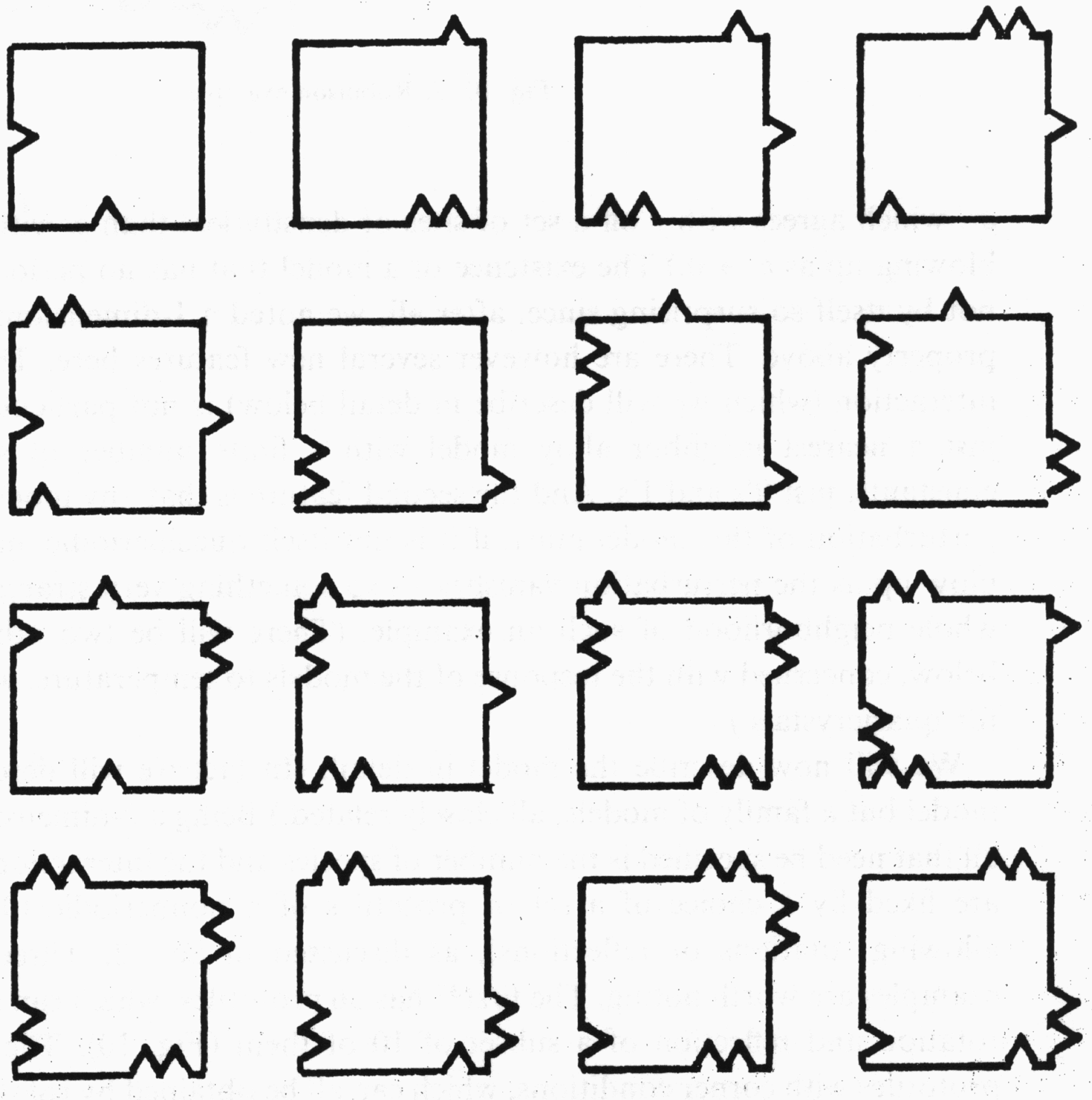


Fig. 12. Ammann's example.

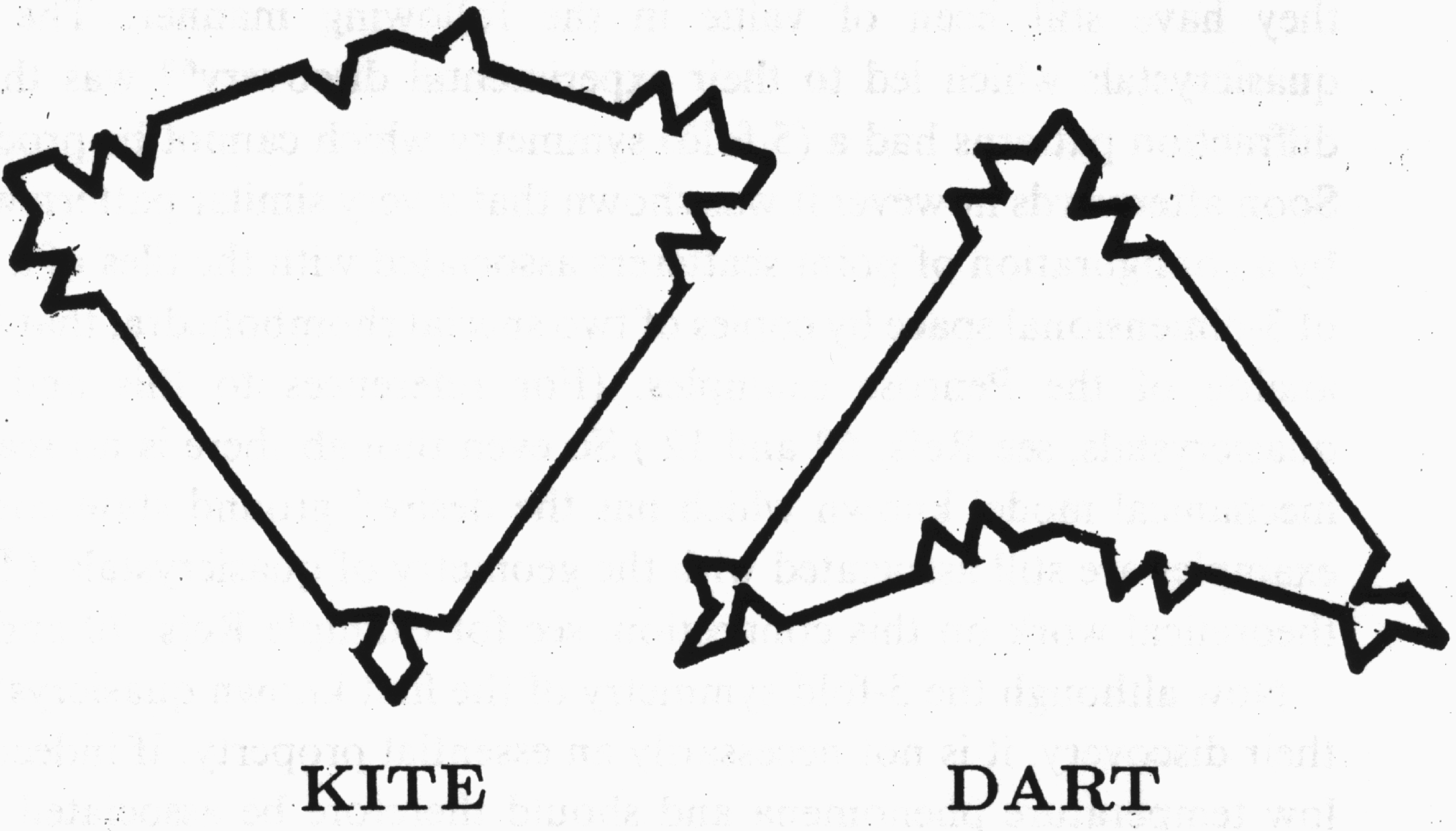


Fig. 13. Penrose's example.

model with the smallest number of species, this is misleading. To clarify this we must recall how our statistical mechanical models are constructed. In particular, we attribute a different species to each of the possible states at a site. If however we attribute a "shape" to the particles, several of the states could be associated with the different orientations of each species. And in fact if the tiling example being used consists of squares with bumps and dents, and as in the first two examples listed above the set of prototiles is generated by rotations and reflections of a smaller subset, it is natural to associate the species with the elements of this smaller set. So in this sense the first tiling example gives rise to a statistical mechanical model with ten species interacting through a nearest neighbor potential, and the second to a model with six species and a next-nearest neighbor potential.

Finally we note that these models have the features we claimed: a nondegenerate quasiperiodic ground state.

It is appropriate at this point to discuss the "Penrose tilings" and their relation to the crystal problem. So far we have only considered generalizations of the tiling problem using essentially square tiles. In an effort to reduce the number of prototiles to a minimum this restriction was abandoned; in this way, and allowing just rotations of the tiles, the smallest set obtained so far contains two prototiles, as in several related examples originally due to Penrose.[36] One of these examples consists of two quadrilaterals, a "kite" and a "dart", with bumps and dents on their edges (Fig. 13). Now how could one use such a tiling example to produce a statistical mechanical model? Of course one could treat the shapes in Fig. 13 as molecules with hard cores and very short range attraction. But this is too artificial: as with the 1-dimensional model noted above,[61] it can put a limit on the generality of crystalline solutions to our basic optimization problem, but it is not convincing evidence that real materials should have such ground states. Unfortunately we know of no reasonable way to make a statistical mechanical model from these Penrose tilings. On the other hand they have still been of value in the following manner. The feature of those quasicrystals which led to their experimental discovery[68] was that their (electron) diffraction patterns had a (5-fold) symmetry which cannot be produced by a crystal. Soon afterwards however it was shown that a very similar pattern would be produced by a configuration of point scatterers associated with the tiles of a nonperiodic tiling of 3-dimensional space by copies of two special rhombohedra, that is, a 3-dimensional analog of the Penrose examples. (For references to this and other models of quasicrystals, see Refs. 69 and 12.) So even though there is no reasonable statistical mechanical model known which has the desired ground state configurations, tiling examples are still associated with the geometry of quasicrystals. (There is interesting theoretical work on this connection: see for example Refs. 70 and 71.)

Now although the 5-fold symmetry of the first known quasicrystals was the key to their discovery, it is not necessarily an essential property. If indeed quasicrystals are low temperature phenomena and should therefore be associated with ground state configurations, the fact that the Penrose tilings are not only similar but isomorphic to tilings by unit squares makes the above alloy models very relevant. (The isomorphism is a bit complicated so we just give a reference: pp. 591ff of Ref. 36. However we note that the isomorphism does not preserve the geometry, just the graph theoretical structure.) In this way the alloy models can play a useful role as toy models for quasicrystals. And in fact they are so used in Ref. 72 where it is shown that if in such a model the chemical potentials are varied, the stoichiometries, that is the relative fractions of each of the constituent species, change abruptly. This behavior, which does not occur in crystals, was therefore predicted for quasicrystals. (Such behavior may have been observed experimentally.[73])

Before we leave these models we wish to address three questions. Do their qualitative features (that is, the forcing of nonperiodicity) depend on: 1) the fact that the interaction has less symmetry than the lattice, for example that it is not invariant under 90 degree rotations; 2) the existence of the underlying lattice; and 3) the zero temperature limit — that is, do the results extend to nonzero temperatures?

The answer to the first question is no. To see this without going into full detail, we will sketch the method of Ref. 74, which is of independent interest. The basic idea is to start with Robinson's example (Fig. 10) of 10 prototiles, each thought of as having side length 4, and define for each of them 16 different unit squares each associated with a position in a prototile (so there is a total of 160 of these unit squares): see Fig. 14. Then an alloy model is built from these unit squares with a fully symmetric interaction of range $5^{1/2}$ such that in any ground state configuration the unit squares are automatically grouped in the groups of 16 "composing" each of the original 10 tiles, and these (large) tiles automatically satisfy the original matching rules. In short, thinking of the original 10 prototiles as molecules, 160 different types of "atoms" are introduced, with a *fully symmetric* interaction, such that in any ground state configuration the atoms automatically group together into the appropriate molecules, which themselves interact (via their constituent atoms) so as to produce nonperiodicity. By the way, it is not hard to modify the above method to produce a model with

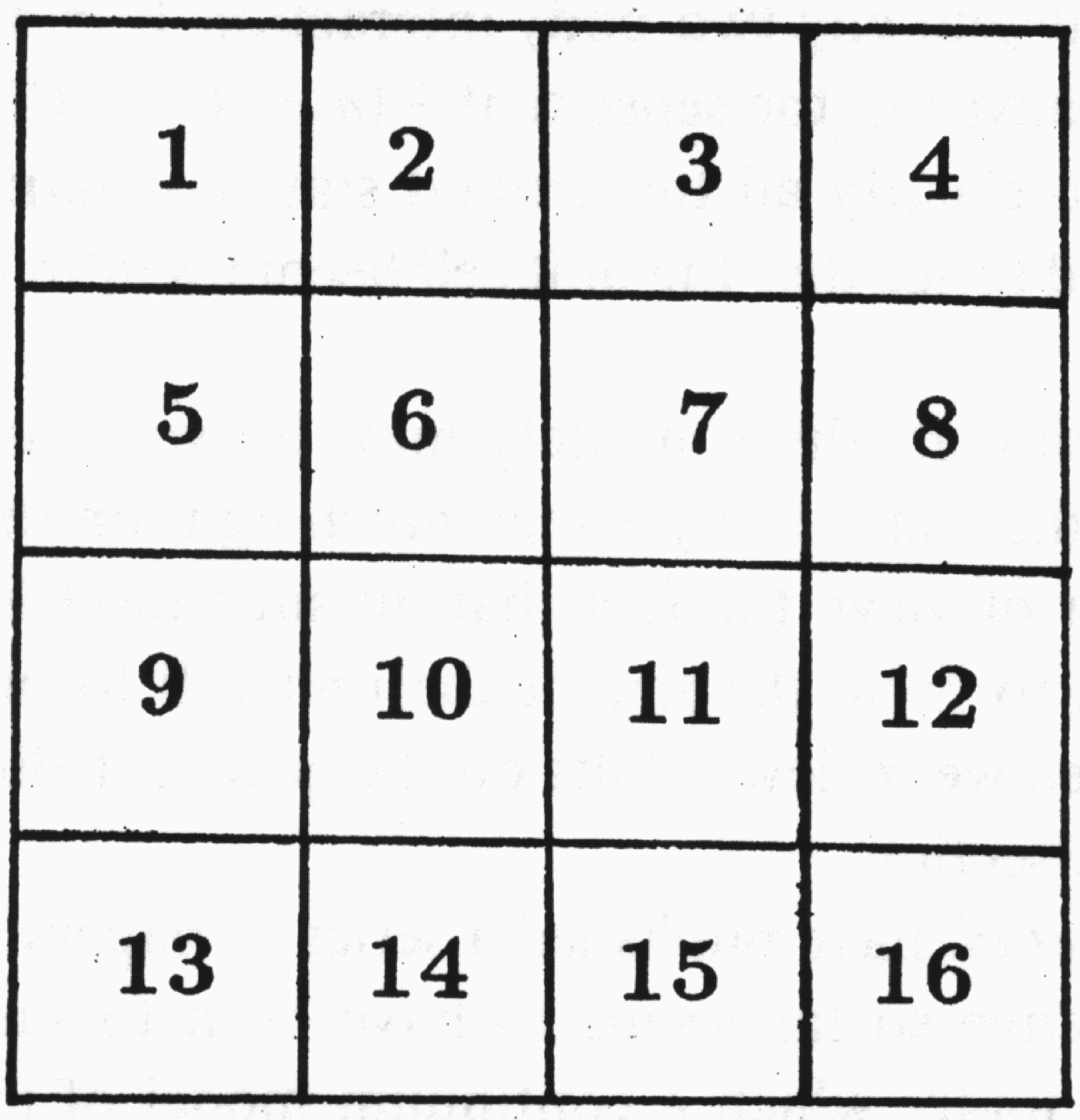


Fig. 14. Atoms 1–16 associated with a molecule; interactions not shown.

an interaction of range 2, that is, next-next-nearest neighbor. This is best possible, since it was previously proven that a fully symmetric interaction which has range less than 2 must have periodic ground state configurations.[46]

The answer to the second question is also no: a continuum model of particles of several species interacting through a finite range, Euclidean invariant potential can still force nonperiodicity. An appropriate model is constructed[65] by combining extended versions of the results in Refs. 64 and 74.

The answer to question 3) is unknown as yet. However Miękisz has modified one of the above alloy models and obtained the following results[75]: either the model has a quasiperiodic equilibrium state at nonzero temperature, or it goes through infinitely many phase transitions as the temperature approaches zero. Obviously in either case the alloy model is behaving in an interesting way, but it is important to determine if the first alternative holds for this or some similar model.

7. Recent Results: General Models

We now graduate to more general results, results valid for a wide range of models.

There is a collection of substances which exhibit modulated or incommensurate structures, for example the 1-dimensional conductor tetracyanoquinodimethane (TCNQ). Presumably because of competing interactions, the underlying crystal structure is modulated by an incommensurate period, thus producing a nonperiodic state. (See Ref. 11 for a good introduction to incommensurates.) Although one can produce (1-dimensional) continuum models with this structure, as in Ref. 61 mentioned in Sec. 6, the simplest models are (1-dimensional) alloy models. For example, consider the class of 1-dimensional, one component lattice gas models with fixed density and any two-body interaction $V = V(x)$ which vanishes at infinity, and is strictly convex in the sense that $V(n+1) + V(n-1) > 2V(n)$ for all $n > 1$. It is not hard to classify all the ground state configurations as a function of the (fixed) density, and to see that the unit cell becomes infinite as the density approaches special values.[76]

Now although these models may be very useful in understanding modulated materials, they have not yet shed much light on the crystal problem. In fact from the latter point of view, the fact that all such models seem to require an infinite range interaction to drive the size of the unit cell to infinity seems artificial. This will be clearer when we review results on the general 1-dimensional alloy model towards the end of this section.

Nijboer *et al.* have published a series of papers[58,77–80] with interesting results. Their main objective so far seems to have been to find general necessary and sufficient conditions under which a continuum model of identical point particles will have a (unique) periodic ground state configuration with a unit cell of 1 particle. They consider purely repulsive potentials (with fixed particle density) and Lennard-Jones type potentials. Most of their results apply only to 1-dimensional models. As an example, they prove that in one dimension if

$$V(x) = \int_0^{+\infty} W(a)\exp(-ax^2)\,da, \quad \text{with } W(a) \geq 0 \text{ and fixed density,}$$

or

$$V(x) = |x|^{-m} - |x|^{-n}, \quad \text{with integers } m > n > 3$$

then among all periodic configurations, the obvious one with a unit cell of one particle has minimum possible energy per particle. In order to extend such results to conclude that this configuration is a ground state configuration, one must also compare it with nonperiodic configurations. This is easily done by means of Sinai's theorem (see Sec. 4) for the Lennard-Jones type potentials,[81] and presumably this technique would also work, in a formalism parallel to that of the DLR for canonical ensembles, to apply to the repulsive potentials. These are interesting results, which contribute to our understanding of the specialization of the crystal problem to crystals with a unit cell of one particle. It would be very useful if they could be generalized to the full problem.

There is an interesting sequence of papers by Duneau and Katz which is related to the crystal problem.[82–85] They emphasize models with finite numbers of particles and prove some general results valid in three (and lower) dimensions. Their main results concern symmetry properties which are attained by energy critical points of N particles; for example, in one dimension, one might hope to prove that a ground state is reflection symmetric about some midpoint. The authors emphasize the need to prove that desirable properties, such as a symmetry, are stable under perturbation of a model. In particular, they first prove that "most" two-body interactions yield nondegenerate critical points for the energy, and that the symmetry of a corresponding critical point configuration (that is, the *rotational* symmetry, for example the reflection symmetry noted above for one dimension, but not any *translational* symmetry since such would be impossible for a finite particle configuration) is stable under perturbation of the interaction. They also prove that for all relevant rotational symmetries, there are open sets of two-body interactions which have energy critical point configurations with that symmetry.

Several remarks are in order. The result that energy critical points (and therefore in particular absolute minima) are generically nondegenerate is useful. (An approach to the concept of degeneracy for infinite particle systems will be discussed below.) It is more difficult than might be thought at first, because perturbations, of a two-body interaction which generates a total energy, produce only very special perturbations of that energy. (It could be argued that the use of classical mechanics and phenomenological forces suggest that many-body interactions be allowed.) But the results on rotational symmetry are less relevant to the crystal problem though they are undoubtedly interesting as mathematics. After all, a crystalline configuration with a complicated unit cell does not have any rotational symmetries, just translational symmetries. Also, the methods used seem to require too large a role for critical points: the results on perturbation cannot distinguish the possibility that under perturbation a true minimum (that is, a ground state configuration) might become a local minimum (that is, an irrelevant configuration).

It should be mentioned that the authors do obtain some results about infinite particle configurations,[84,85] and ground state configurations, but these do not represent as much of an advance on previous work as do the results discussed above.

A different set of ideas was put forth in Refs. 46 and 47, in connection with the construction called "fraction space" (see Sec. 4), whose main objective is to develop a useful notion of degeneracy for ground states. (The relevance of degeneracy to the crytal problem is clear from the last paragraph of Sec. 5.) In the same vein as the discussion in Sec. 4 on "mixing", assume we are working with an alloy model with interaction V and let f be a periodic configuration. Define the discrete probability distribution μ_f as the average over a unit cell of f of the translates of the point mass concentrated at f. Let $e^V(f)$ denote the energy density of f and define e^V as the infimum of the $e^V(f)$ over all periodic f. Finally define R_n^V, for each positive integer n, as the set

$$\textit{weak-}{*}\ \textit{closure}\left\{\mu_f \middle| \textit{periodic } f \textit{ such that } e^V(f) < e^V + \frac{1}{n}\right\}.$$

The intersection $\bigcap_{n\geq 1} R_n^V$ is easily seen to be nonempty by compactness. The key idea of this line of development is embodied in the following definition: the interaction V is *nondegenerate* if and only if this intersection contains exactly one element, and in that case we denote the unique element by μ^V. Intuitively, an interaction is nondegenerate if it has a unique translation invariant zero temperature state, but technically it is required that this state be approximable by averages of periodic states in a certain useful way (in the spirit of Fourier analysis of functions).

Examples of nondegenerate models are any of the models defined above by tiling examples, and also the 2-dimensional one component lattice gas with nearest neighbor repulsion and any chemical potential. An example of a degenerate model is the corresponding lattice gas model with an attractive interaction, and critical chemical potential (*i.e.* on the phase transition line). In fact any interaction (remember that fixed values of chemical potentials are included in the interaction) which at zero temperature has more than one phase is degenerate.

The first result using these ideas[47] holds for alloy models in any dimension, and refers to the Banach space I of interactions which is defined in Sec. 4. The result contains two parts: a) The intersection $\bigcap_{n\geq 1} R_n^V$ contains all possible ground states for V; and b) Among all interactions V in I, a generic subset (that is, a subset containing a countable intersection of dense open sets) of them are nondegenerate.

Part a) shows that in fact all ground states are approximable in the desired way, and part b) shows that all but a negligible set of interactions are nondegenerate. In a sense this result is a weak, zero temperature form of the Gibbs phase rule, since it implies that for most interactions there is a single phase. But really it is much more than that because it shows that the unique phase is approximable in a very useful way.

The other result which uses these ideas[86,87] holds for alloy models in dimension one only. It also has two parts: a) If the interaction V is finite range and nondegenerate then μ^V is the average of a periodic state over a unit cell — an immediate consequence is that such a model satisfies the Third Law of Thermodynamics — and b) Among interactions V of finite range $\leq R$, R arbitrary but fixed, "most" are nondegenerate, where "most" can mean either generic as above, or, "all but measure zero" in the usual sense. Together, it follows that all but a negligible set of (1-dimensional) alloy models have unique, crystalline ground states, and therefore satisfy the Third Law of Thermodynamics.

Three comments are in order about this result. First, it does not follow from part b) of the previous result because the set of interactions of finite range is itself negligible in I. Second, it is not just an existence proof: there is a constructive way to determine if a given interaction is nondegenerate since the proof gives a (nonoptimal) finite upper bound on the period of the unit cell in terms of the range R and the number of species in the model, and then there is a constructive way to determine the ground state. And finally, it calls into question the relevance of "models" of 1-dimensional quasicrystals.

8. Summary

Perhaps the foremost area of research in statistical physics is directed toward understanding the qualitative phase diagram of ordinary matter: the existence of, and transitions between, the gas, liquid and solid phases; see Chap. VIII in Ref. 88, Ref. 89 and p. 103 in Ref. 16. The theory of the liquid-gas transition, following from the theory of van der Waals on the one hand, and the work of Peierls and Onsager on the Ising model on the other hand, is still far from satisfactory. But in contrast the theory of the fluid-solid transition is basically nonexistent, in part because of a lack of understanding of the fundamental nature of solids; see pp. 15–17 in Ref. 4. This article is a review of work on the "crystal problem", a necessary ingredient in understanding the nature of solids.

So what is the status of research on the crystal problem? The few indisputable steps forward seem to be the following.

First, we have a reasonable mathematical statement of the problem, which is convincing in its relevance and depth partly because of its relation with traditional models and partly because of its intimate connections with the sphere packing and nonperiodic tiling problems of mathematics: the packing, tiling and crystal problems are shown above to be not just vaguely similar, but essentially identical. As part of this "step" we include our present understanding of the results of, and interrelations between, the various historical approaches to the problem, and the relevance of the order-disorder phenomenon of alloys.

Second, the models based on nonperiodic tiling examples, whether or not they are relevant to quasicrystals, are a sobering challenge to conventional wisdom and seem to represent an essential aspect of the problem. This is supported in four ways: 1) the similarity of these to traditional models, that is, their ordinariness; 2) the response of the models to small perturbations; 3) the low temperature behavior of the models; and 4) their connection with quasicrystals.

And finally, the circle of ideas surrounding the notion of nondegeneracy, and the full solution of the 1-dimensional problem, are the first steps toward a general theory. In conjunction with the quasiperiodic (tiling) models in higher dimensions, they prove that there is a dimensional dependence in the ability of energy to force (crystalline) order which is in direct opposition to the dimensional dependence of the ability of entropy to destroy it.

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