Entropy of a three-dimensional random-tiling quasicrystal

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A numerical calculation of the entropy of a three-dimensional randomly rearranged Penrose tiling is described. The entropy per tile is obtained to be 0.24±0.02.

Recent experimental and theoretical work has focused attention on the random-tiling model for quasicrystal structure.[1,16] In this model it is suggested that quasicrystals may be analogous to a random rearrangement of the well-known Penrose tiling. The Penrose tiling is the prototype for the quasiperiodic-crystal model.[17] Two- and three-dimensional versions of the random-tiling model have been explored numerically in recent publications and have been shown to possess the Bragg peaks characteristic of long-range translational order.[10–13,15,16,18] Here we report a calculation using Monte Carlo simulation of the entropy of three-dimensional random tilings of space by the Penrose rhombohedra. This calculation is in the spirit of the calculation for two-dimensional random tilings by Orrick.[19]

The calculation exploits the standard relationship between the entropy and specific heat:

$$T\frac{dS}{dT}=\frac{dE}{dT}=C(T)=\frac{\langle E^2\rangle-\langle E\rangle^2}{k_B T^2}\qquad(1)$$

(where k_B is Boltzmann's constant) and the fact that the ensemble of random tilings will be the high-temperature limit for essentially any choice of interaction between the tiles as long as the space-filling constraint is maintained. The entropy of the random tiling is obtained by integrating the specific heat divided by temperature from $T=0$ to ∞, or, equivalently, by integrating the specific heat as a function of the logarithm of temperature over all temperatures:

$$S(\infty)-S(0)=\int_0^\infty\frac{C(T)}{T}dT=\int_{-\infty}^\infty C(T)\,d\ln T\ .\qquad(2)$$

In these simulations we impose the Hamiltonian

$$H=J\sum_{i=1}^N |x_i^\perp|^2\ ,\qquad(3)$$

where $x^\perp$ is the perpendicular-space coordinate of the ith vertex and the sum runs over all the vertices of the tiling.[17] The perpendicular-space coordinates are defined by the following procedure (illustrated in Fig. 1 for a two-dimensional tiling). Choose a site as the origin. Define the six integers $\{n_\alpha\}$ for each other site by counting the signed number of steps from the origin to the site in question along each of the six directions defined by

$$\hat{e}_\alpha^\parallel=(\cos(2\pi\alpha/5),\sin(2\pi\alpha/5),1\sqrt5)\ \text{for}\ \alpha=0,\ldots,4\ ,$$

$$\hat{e}_5^\parallel=(0,0,1/\sqrt5)\ .\qquad(4)$$

The perpendicular-space coordinate is the three-dimensional vector given by

$$x^\perp=\sum n_\alpha\hat{e}_\alpha^\perp\ ,\qquad(5)$$

where $\hat{e}_\alpha^\perp=(\cos(4\pi\alpha/5),\sin(4\pi\alpha/5),1/\sqrt5)$ for $\alpha=0,\ldots,4$,

$$\hat{e}_5^\perp=(0,0,-1/\sqrt5)\ .$$

Because we are interested only in the entropy difference between zero and infinite temperature, the specific choice of the Hamiltonian is of no physical significance and may be chosen for computational convenience. Because there is no phase transition in the system described by the Hamiltonian (3) there is little size dependence in the temperature region where $C(T)/T$ is substantial. The entropy may be determined reasonably accurately using simulations of relatively small systems.

The systems actually used in the simulations were finite periodic approximants to the quasiperiodic tiling of sizes 188 and 796 tiles. The simulation moves consisted of "flips" of rhombic dodecahedra composed of four tiles
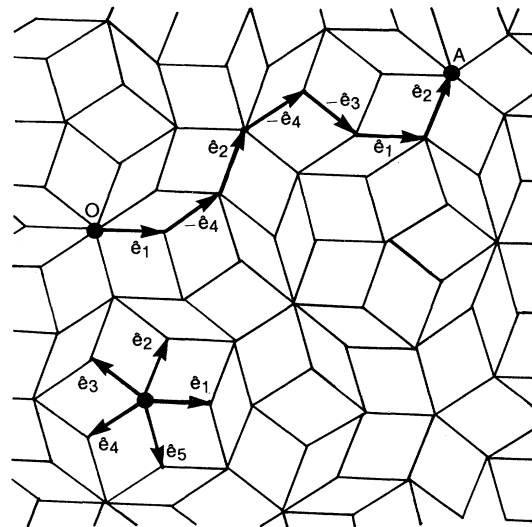

FIG. 1. Illustration of the method of defining higher-dimensional coordinates for a two-dimensional random tiling. An exactly analogous method was used in the three-dimensional calculations.

(two oblate rhombohedra and two prolate rhombohedra). This tile rearrangement is analogous to the hexagon flip used to disorder two-dimensional Penrose tilings. A typical run at each temperature consisted of $5000N$ attempted flips, where N is the number of rhombohedral tiles.

The specific heat was generated by calculating the average energy fluctuations. In order to perform the integrations, a smoothing-spline fit was applied to the specific-heat curve as a function of the logarithm of temperature. The integration was then performed on the corresponding spline. Similar results were obtained by fitting a spline to the energy-versus-temperature plot and then differentiating the resulting spline in order to obtain the specific heat. The smoothing-spline program was a standard package that minimizes the quantity

$$\varepsilon = \Sigma(\, AK_i^2 + \sigma_i^2\,) \,, \tag{6}$$

where K_i is the local curvature near a particular temperature and σ_i^2 is the local squared deviation of the fit near that temperature. The constant A was adjusted by eye to obtain a reasonable fit and then varied to assign an error bar to the corresponding entropy value.

Figure 2 shows the energy as a function of temperature for approximant with $N=188$ and 796 particles. Figure 3 displays the specific heat for these same two systems. There is clearly little size dependence in the peak region. Spline fits to the data from the two sizes of system are shown in Fig. 4. Integrating these fitted splines leads to a value for the entropy of $S/k_B = 0.24 \pm 0.02$ (where the error bar is computed by fitting splines to the separate data sets for each system size). This value is comparable to the values of 0.4810 for the directly analogous two-dimensional random tiling[16] and 0.2374 for the two-dimensional binary random tiling.[13]

Unfortunately we are unable to supply at this time a direct comparison between this entropy and the entropy change involved in the experimental transition from crystal to quasicrystal. Several considerations apply if one were to attempt to compare this value with experimental values for the entropy difference between the icosahedral
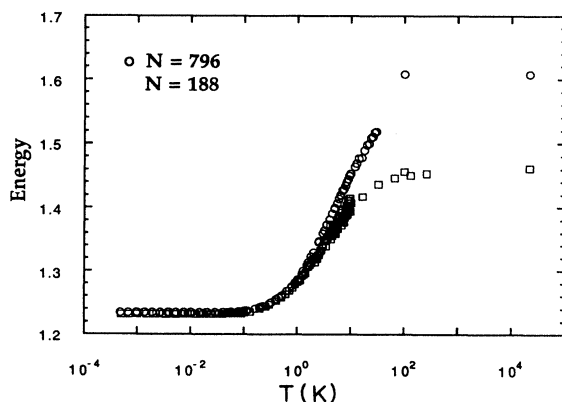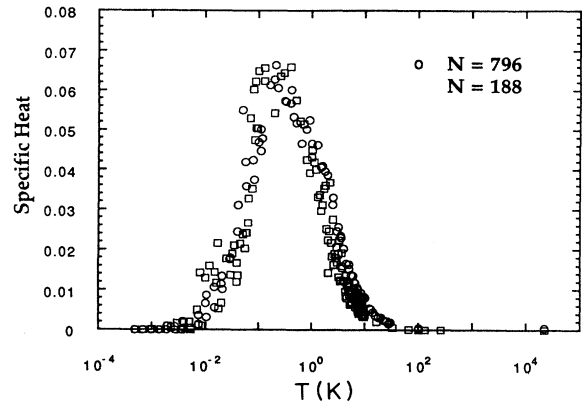

FIG. 3. Specific heat as a function of temperature for systems of size $N=188$ and 796 tiles.

phase and the corresponding crystal phases:

(i) Even if the icosahedral materials are appropriately described with a random-tiling model, the particular version of random tiling may not correspond to the fully random model studied here. Note, for example, the

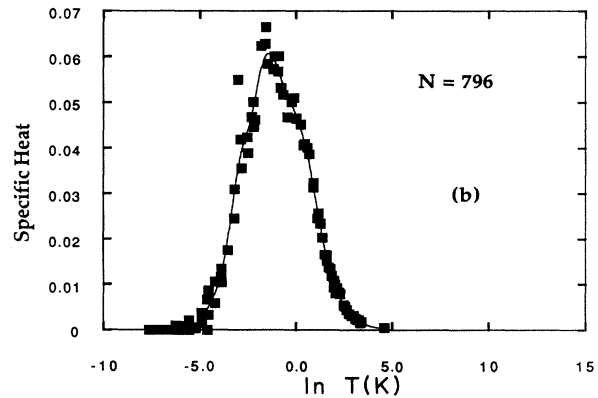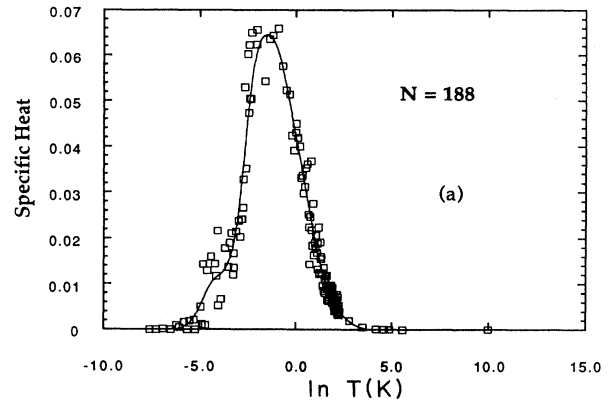FIG. 2. Energy as a function of temperature for systems of size $N=188$ and 796 tiles.

FIG. 4. Specific heat as a function of logarithm of temperature and the spline fits to this simulation data for (a) $N = 188$ and (b) $N = 796$ tiles.

difference in entropy for binary and fully random tilings in two dimensions. However, we expect the order of magnitude to be correct.

(ii) The entropy we have computed is the entropy per tile. In order to compare with experimental entropy values an estimate of the number of atoms per tile is required. Thus a particular atomic decoration must be invoked.

(iii) If the crystal to be compared to the icosahedral phase is a complicated approximant structure, then some phason-type rearrangements are likely to be of importance in the crystal also, so that the entropy difference might be significantly lower than the value computed here. Indeed, it is known that there is little heat released in the transition from icosahedral Al-Cu-Fe to the lower-temperature crystalline phase (which is a structure with a complicated unit cell), while there is a substantial heat release in the transformation of Al-Cu-Ru to its low-temperature phase (which has a relatively simple crystal structure).[20]

(iv) Other contributions to the entropy difference, such as differences in vibrational entropy, must also be taken into account.

In the future, as more experimental information becomes available, and as other theoretical calculations are made, one may hope to use the information obtained here in understanding the stabilization of the quasicrystal phase.

[1] P. A. Bancel, Phys. Rev. Lett. **63**, 25 (1989).

[2] S. E. Burkov (unpublished).

[3] H. Chen, S. E. Burkov, Y. He, S. J. Poon, and G. J. Shiflet, Phys. Rev. Lett. **65**, 72 (1990).

[4] V. Elser, in *Icosahedral Structures,* edited by M. V. Jaric (Academic, San Diego, 1989).

[5] C. A. Guryan, A. I. Goldman, P. W. Stephens, K. Hiraga, A. P. Tsai, A. Inoue, and T. Matsumoto, Phys. Rev. Lett. **62**, 2409 (1989).

[6] C. L. Henley, in *Quasicrystals and Incommensurate Structures in Condensed Matter,* edited by M. J. Yacaman, D. Romeu, V. Castaño, and A. Gómez (World Scientific, Singapore, 1990), p. 152.

[7] K. Hiraga, B. P. Zhang, M. Hirabayashi, A. Inoue, and T. Masumoto, Jpn. J. Appl. Phys. Pt. 2 **27**, L951 (1987).

[8] A. R. Kortan, R. S. Becker, F. A. Thiel, and H. S. Chen, Phys. Rev. Lett. **64**, 200 (1990).

[9] P. W. Leung, C. L. Henley, and G. V. Chester, Phys. Rev. B **39**, 446 (1989).

[10] K. J. Strandburg, L.-H. Tang, and M. V. Jaric, Phys. Rev. Lett. **63**, 314 (1989).

[11] K. J. Strandburg, Phys. Rev. B **40**, 6071 (1989).

[12] L. -H. Tang, Phys, Rev. Lett. **64**, 2390 (1990).

[13] M. Widom, D. P. Deng, and C. L. Henley, Phys. Rev. Lett. **63**, 310 (1989).

[14] M. Widom, K. J. Strandburg, and R. H. Swendsen, Phys. Rev. Lett. **58**, 706 (1987).

[15] L. Shaw, V. Elser, and C. L. Henley, Phys. Rev. B **43**, 3423 (1991).

[16] L. Shaw and C. L. Henley, J. Phys. A (to be published).

[17] P. J. Steinhardt and S. Ostlund, *The Physics of Quasicrystals* (World Scientific, Singapore, 1987).

[18] M. Widom, in *Proceedings of the Anniversary Adriatico Conference– Quasicrystals, Trieste, Italy,* edited by M. V. Jaric and M. Ronchetti (World Scientific, Singapore, 1989).

[19] W. P. Orrick, B. S. thesis, Princeton University, 1986 (unpublished).

[20] A. Goldman (private communication).