Vibrational properties of small two-dimensional classical crystals

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Quasiharmonic crystals have long provided useful data for developing perturbation treatments of more realistic materials.[1] The lattice-dynamics model, even when restricted to nearest-neighbor interactions and to close-packed crystal lattices, has been very useful in elucidating the equilibrium thermoelastic statistical mechanics of real three-dimensional crystals.[2] The detailed frequency spectrum of the elastically isotropic two-dimensional triangular lattice, including the contributions of free-surface Rayleigh waves,[3] was worked out a decade ago.

The computational treatment of two- or three-dimensional crystals is simplest when periodic boundary conditions are used. In this case the N-particle equations of motion, in D dimensions, can be solved by diagonalizing a set of N D-dimensional matrices, where each matrix corresponds to a set of D normal-mode vibrations.[1] For the two-dimensional triangular lattice, this approach was followed over 20 years ago, leading to quantitative relations for the number dependence of the vibrational entropy[4] and mean-squared displacement:[5]

$$\Delta S/Nk \approx 0.273\ 26 - (1/N)\ln N;$$

$$\langle r^2\rangle/r_E^2 \approx 0.367\ 55\ \ln N.$$

The entropy and mean-squared displacement are both given relative to the predictions of the single-frequency Einstein model, and apply to the stress-free case. The two constants, available with five-figure accuracy from extrapolated computer simulations, were ultimately evaluated exactly.[5,6]

During the past 20 years the simulation of transport properties in two dimensions, hampered by relatively large long-lived fluctuations, has finally led to the suggestion that finite coefficients can be defined, even in the large-system limit,[7] despite the apparent divergence of the corresponding Green–Kubo expressions for these properties.[8] Though the fluid results are still puzzling, the logarithmic divergence of particle vibrations, with size, is certainly well-understood, at least with periodic boundaries.[5] The rigid-boundary case is much more demanding, from the computational standpoint, as the full dynamical matrix, $2N\times 2N$, needs to be diagonalized to find the quasiharmonic properties. Nevertheless, computers today are quite capable of diagonalizing matrices with several million matrix elements.

We have evaluated and diagonalized the dynamical matrices for a series of close-packed structures, all with the maximally symmetric hexagonal structure: 1, 7, 19, 37,..., $3n^2-3n+1$,..., 2107 particles, embedded into a confining crystal of fixed particles. The seven-atom hexagon ($n=2$), e.g., interacts with 12 additional fixed atoms, which surround it. The last calculation ($n=27$), corresponds to a hexagonal crystallite, 27 atoms on a side, and confined by $6n=162$ neighboring atoms. The 4214 vibrational frequencies were evaluated as eigenvalues of the corresponding 4214×4214 matrix.

For all 27 cases both the entropy and the mean-squared displacement were measured, relative to the simplest ($n=N=1$) Einstein model prediction. The results are shown in Table I. These numerical data can be described by the following approximate relations, for large N:

$$\Delta S/Nk = 0.273 - O(N^{-1/2});$$

$$\langle r^2\rangle/r_E^2 = 0.35_6\ \ln N + O(\ln N/N^{1/2}).$$

The entropy result agrees with the known periodic case, confirming that thermodynamic quantities are independent of the boundary details for sufficiently large systems. The displacement data, on the other hand, establish that the relatively large role played by fluctuations and boundary conditions in two dimensions affects the coefficient of the logarithmic di-

TABLE I. Vibrational entropy and mean-squared displacement, relative to the predictions of the single-oscillator Einstein model, are listed for hexagonal crystallites of $3n^2-3n+1$ nearest-neighbor Hooke's Law particles embedded in a rigid hexagon of $6n$ fixed particles.

n	N	$\Delta S/Nk$	$\langle r^2\rangle/r_E^2$
1	1	0.000 00	1.000 00
2	7	0.110 15	1.265 99
3	19	0.159 37	1.464 18
4	37	0.185 69	1.615 89
5	61	0.202 03	1.738 80
6	91	0.213 17	1.842 34
7	127	0.221 25	1.931 94
8	169	0.227 40	2.011 01
9	217	0.232 23	2.081 83
10	271	0.236 14	2.146 01
11	331	0.239 35	2.204 71
12	397	0.242 05	2.258 82
13	469	0.244 35	2.309 01
14	547	0.246 33	2.355 83
15	631	0.248 05	2.399 72
16	721	0.249 57	2.441 01
17	817	0.250 91	2.480 02
18	919	0.252 11	2.516 98
19	1027	0.253 18	2.552 10
20	1141	0.254 15	2.585 56
21	1261	0.255 03	2.617 51
22	1387	0.255 83	2.648 09
23	1519	0.256 57	2.677 40
24	1657	0.257 240	2.705 555
25	1801	0.257 861	2.732 638
26	1951	0.258 436	2.758 729
27	2107	0.258 969	2.783 901

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vergence significantly, changing it from 0.368 to 0.35_6, but without changing the functional form established in the periodic case. White's experimental fluid data, cited in Ref. 5, determine this coefficient within an uncertainty of 15%.

It may well seem strange that large-crystal rms fluctuations can depend upon crystal size much more strongly than does the entropy. There is a simple analog in one dimension.[9] Though the limiting [convergent] large-crystal entropy per particle is the same for rigid and for periodic boundaries, the [divergent, proportional to N] rigid-boundary mean-squared displacement approaches twice the periodic value for large N. Two-dimensional problems lie mostly beyond the reach of analysis.[10]

This work on two-dimensional crystallites was stimulated by correspondence with Bocquet (Lyon) who is studying the dependence of two-dimensional transport properties on the boundary conditions using mode-coupling theory and nonequilibrium molecular dynamics. We hope that continuing advances in computational capacity and speed will make it possible to compare these crystalline results with accurate large-system viscosities within the next few years.

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