

72
73

Analytic and numerical surface dynamics of the triangular lattice

William G. Hoover, Anthony J. C. Ladd, Donna Friesen,^{a)} and Bill Moran

Department of Applied Science, University of California at Davis, Davis, California 95616
(Received 24 November 1981; accepted 7 December 1981)

The high-frequency surface waves discovered by Allen, Alldredge, and de Wette, in numerical studies of three-dimensional fcc crystals, have two-dimensional analogs. Analytic solutions of the equations of motion for two-dimensional close-packed lattices reveal a high-frequency surface-mode branch linking together the high-frequency and low-frequency bulk-mode bands. The dispersion relation for this branch is used to estimate the surface entropy. The estimate agrees well with Carman and Huckaby's recent cell-cluster calculation. Both the dispersion-relation and cell-cluster surface entropy estimates lie slightly below an accurate value we obtain here by extrapolating small-crystal entropies to the thermodynamic limit.

Surface, or "Rayleigh," waves were first applied to understanding the seismic structure of the earth. Today, much smaller scale technological applications to microwave transmission on semiconductor surfaces are being actively pursued. The theory of surface waves, first developed for macroscopic continua and later extended to layered media and to microscopic crystals including the effects of stress and defects, has led to only a few numerical calculations.¹ The first relatively complete study, for a three-dimensional close-packed crystal, was carried out by Allen, Alldredge, and de Wette ten years ago.² This work revealed several high-frequency branches of surface waves localized near crystal faces. The complexity of the results precluded much theoretical analysis.

The frequency changes induced by surfaces have an impact on thermodynamic properties. The enhanced specific heat of powders is conventionally explained in this way. For recent calculations of ionic-crystal surface modes and thin-film specific heats, see Ref. 3. In three dimensions, analytic work is complicated by the intricate structure of the surface modes.

The high-frequency modes found in three dimensions suggested that similar excitations probably exist in two-dimensional crystals, where analytic work is practical. We took up this question by studying the dynamics of finite periodic strips of close-packed triangular lattice, with and without two parallel free boundaries in the direction of the close-packed rows. These strip calculations, detailed in Table I, could be analyzed for modes localized near the surfaces and could also be used to estimate the surface entropy contribution s_s to the excess entropy

$$S^e = S - S_{\text{Einstein}} = Ns_b + N_s s_s, \quad (1)$$

where N is the number of particles in the crystal, N_s is the number of particles on the surface, and the characteristic per particle entropies s_b and s_s are large-crystal limiting values. Huckaby⁴ calculated the limiting bulk entropy $s_b/k = 0.27326$ analytically, from Dean's⁵

dispersion relation for the triangular nearest-neighbor lattice. The numerical data in Table I give the estimate for the surface entropy $s_s/k = 0.6607$. The surface entropy was already known approximately from three different kinds of calculations.⁶⁻⁸ It was estimated from numerical studies of crystals with free boundaries by evaluating the determinants of the corresponding force-constant matrices. This approach gave 0.66 for two different crystal shapes, equilateral triangles, and regular parallelograms. This result was consistent with the entropy associated with the surfaces of brittle cracks.⁷ Recently, Huckaby, Carman, and Kincaid^{8,9} have applied the cell-cluster theory to the surface and crack problems. Their estimate is slightly lower, 0.62. Our present results are sufficiently accurate, even though limited to crystals of only a few hundred particles, to confirm the accuracy of the free-boundary studies.

The dynamical vibrations of the triangular lattice revealed short wavelength surface modes independent of crystal size. These modes were (1) the well-known Rayleigh wave mode with a wavelength of two interparticle spacings $\lambda = 2d$ and (2) a second higher-frequency mode at the same wavelength. The displacements to which these modes correspond are illustrated in Fig. 1. The numerical work showed that the ratio of the two frequencies is *exactly* $(3 + \sqrt{3})/\sqrt{6}$, even in narrow strips.

Our previous analysis of Rayleigh waves in the triangular lattice¹ had established that the dispersion relation was a solution of the quadratic equation

$$(m\omega^2/\kappa)^2 - 6 \sin^2(kd/2)(m\omega^2/\kappa) + 6 \sin^4(kd/2) = 0, \quad (2)$$

where the wave vector k is $2\pi/\lambda$. The Rayleigh waves correspond to the low-frequency solution $\omega_R = [(3 - \sqrt{3}) \times (\kappa/m)]^{1/2} \sin(kd/2)$. The other higher-frequency solution was ignored because it did not satisfy the stress-free surface boundary condition at long wavelengths. When our present numerical work revealed a size-independent mode with wavelength $2d$ and frequency $\omega' = [(3 + \sqrt{3})(\kappa/m)]^{1/2}$ we re-examined the solutions of Eq. (2). We found that the high-frequency wave was a part of a branch $\omega' = [(3 + \sqrt{3})(\kappa/m)]^{1/2} \sin(kd/2)$ which spanned a narrow range of wavelengths with $|(\pi/2) - (\pi d/\lambda)| \leq \cos^{-1}(3/4)^{1/4} = 0.37473$. This branch smoothly con-

^{a)}Supported by the Academy of Applied Science under a grant from the United States Army Research Office, Research Triangle Park, North Carolina.

TABLE I. Entropies for $L \times L$ triangular-lattice crystals. The crystal shapes are all regular parallelograms, either periodic or with parallel free boundaries (making a periodic strip L atomic rows high). For both types of crystals the sums, over all $2N-2$ vibrational frequencies, $(1/N) \sum \ln(\nu_E/\nu) \equiv S^e/Nk$, are tabulated. The difference between the free and periodic sums multiplied by $L/2$ gives the reduced per particle surface entropy s_s/k . In the triangular lattice, the Einstein frequency ν_E is related to the atomic mass m and interatomic force constant κ by the relation $(2\pi\nu_E)^2 = 3\kappa/m$.

L	S^e/Nk for parallelograms		
	Free	Periodic ^a	s_s/k
2	0.238 693	-0.107 881	0.346 574
3	0.315 236	0.005 791	0.464 169
4	0.342 672	0.083 240	0.518 864
5	0.352 284	0.132 478	0.549 515
6	0.354 543	0.164 864	0.569 036
7	0.353 578	0.187 120	0.582 602
8	0.351 191	0.203 038	0.592 611
9	0.348 222	0.214 817	0.600 320
10	0.345 075	0.223 786	0.606 447
11	0.341 950	0.230 779	0.611 438
12	0.338 942	0.236 345	0.615 584
13	0.336 095	0.240 851	0.619 084
14	0.333 423	0.244 554	0.622 079
15	0.330 926	0.247 637	0.624 670
16	0.328 600	0.250 233	0.626 936
17	0.326 433	0.252 440	0.628 933
18	0.324 413	0.254 335	0.630 706
19	0.322 531	0.255 974	0.632 292
20	0.320 773	0.257 401	0.633 719
21	0.319 131	0.258 654	0.635 009
∞	0.273 26 ^b	0.273 26 ^b	0.660 72 \pm 0.000 05 ^c

^aValues for $L = 3, 4, \dots, 15$ consistent with these are given in Table III of A. Beyerlein and Z. W. Salsburg, *J. Chem. Phys.* 47, 3763 (1967).

^bSee Ref. 4.

^cThe estimate is based on a fit of the form $a + b e^{c/L} + (d/L) + (f/L) e^{g/L}$, where $a, b, c, d, f,$ and g are constants.

nects the longitudinal and transverse dispersion relations for waves parallel to the close-packed direction, as is shown in Fig. 2.

Both the high-frequency and the low-frequency Rayleigh waves (R' and R in Fig. 2) correspond to similar vibrations. The atomic trajectories are ellipses. At the special value $k = \pi/d$, these ellipses degenerate into straight-line trajectories parallel and perpendicular to the crystal surface. The high-frequency surface solutions all resemble the maximum-frequency degenerate case shown in Fig. 1, but smoothly become linear com-

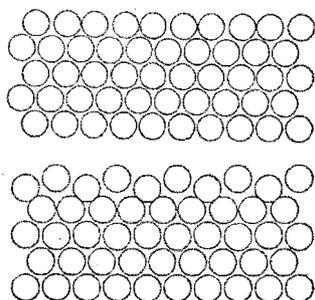


FIG. 1. Displacements of particles for high-frequency (top) and low-frequency (bottom) surface waves. Both waves correspond to the same wavelength $\lambda = 2d$. In each case, the amplitudes decrease exponentially with penetration depth into the crystal.

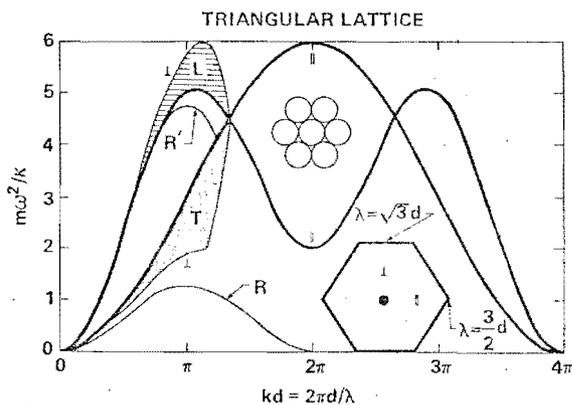


FIG. 2. Dispersion relations in the two-dimensional triangular close-packed crystal. The relative orientation of particles in the crystal (indicated as circles in the center of the figure) and the first Brillouin zone (the heavily outlined hexagon at the base of the figure) are shown. The symbols \parallel and \perp are used to indicate waves propagating parallel and perpendicular to the direction of the close-packed lines of atoms. The atomic mass is m . The interparticle spacing is d . The Hooke's Law force constant of the springs linking neighboring pairs of particles is κ . The heavy curves correspond to the longitudinal and transverse waves parallel to the close-packed direction. The shaded regions include all high-frequency and low-frequency waves included in the first Brillouin zone for any propagation direction (bulk waves). The Rayleigh wave solutions, both the low-frequency R and the high-frequency R' branches, are shown. The high-frequency branch links the high-frequency L and low-frequency T bands together.

binations of high-frequency bulk waves at the two intersections with the bulk bands. It is interesting to note that for values of $\pi d/\lambda$ greater than $\cos^{-1}(3/4)^{1/4}$, the low-frequency Rayleigh wave solution becomes complex. Details of the calculation of both dispersion relations are similar and the analysis is described in Ref. 1.

Both the high-frequency and the low-frequency surface waves affect the surface entropy. A quantitative estimate can be based on the entropy change associated with the conversion of two waves, parallel to the close-packed direction, into (i) an ordinary low-frequency Rayleigh wave, and (ii) either a high-frequency surface wave described by Eq. (2) or an ordinary bulk wave. The average entropy of the longitudinal and transverse bulk waves, $0.274 65 \times 2k$ per particle on the surface, is replaced by the sum of (i) and (ii)

$$(1.123 75k) + (-0.238 56$$

$$\times 0; 204 07k + 0.761 44 \times 0.136 63k) = 1.179 1k,$$

giving an increase of $0.630k$ for each surface particle, in good agreement with the cell-cluster work,^{8,9} but definitely inconsistent with the accurate data shown in Table I. The discrepancy of $0.03k$ between the approximate surface-entropy estimate just described and the accurate value $0.6607k$, is intriguing.

We know of no rigorous proof that the surface entropy exists in two dimensions. Our attempts to bound this entropy, using the Gibbs-Bogolyubov free-energy inequality $A \leq A_0 + \langle E - E_0 \rangle_0$ have been only partially successful. By considering a periodic-boundary reference crystal with Helmholtz free energy A_0 , and treating the

effect of *removing* the $2L$ nearest-neighbor bonds spanning a new surface as a perturbation, s_s can be bounded. The perturbed crystal has two surfaces of total length $2Ld$, and the perturbation energy $\langle E - E_0 \rangle_0$ is $-2LkT/3$ in this case, using equipartition. This establishes that the surface entropy per particle s_s exceeds $k/3$. An attempt to bound the entropy from above, by using the free-boundary system as reference, establishes only that s_s cannot exceed a value of order $k \ln N$. The logarithmically divergent bound results from the logarithmic divergence of the mean-squared displacement characteristic of two-dimensional crystals.

Because the Gibbs-Bogolyubov bounds, as well as approaches based on Kirkwood's coupling-parameter theory, suggest the possibility of divergence, either as $\ln N$ or as $\ln \ln N$, we have attempted to fit the numerical data for the $L \times L$ crystals with functional forms incorporating these divergences. We found that the coefficients vary widely with the range of the data included and conclude therefore that the two-dimensional surface entropy does indeed have a well-defined nondivergent shape-independent value. A simple explanation of that value expressed in terms of the dispersion relations for the bulk and surface modes is still lacking and remains a tantalizing puzzle.

In carrying out this work, we have profited from many stimulating conversations with John Wheeler [who

pointed out that the Rosenstock--Newell model has a nondivergent surface entropy and pointed out the related work of M. E. Fisher and G. Caginalp, *Commun. Math. Phys.* 56, 11 (1977)] and Dale Huckaby (whose cell-cluster calculations accompany this work). Wheeler and Prais expect soon to publish modified-moment estimates of the triangular-lattice surface entropy.

¹For references, see A. J. C. Ladd and W. G. Hoover, *Phys. Rev. B* 24, 6889 (1981).

²R. E. Allen, G. P. Alldredge, and F. W. de Wette, *Phys. Rev. B* 4, 1648, 1661, 1682 (1971). For a novel numerical approach, see M. Prais, Ph.D. dissertation, University of California at San Diego, 1981.

³T. S. Chen, G. P. Alldredge, and F. W. de Wette, *Surf. Sci.* 62, 675 (1977); P. Mazur, *Phys. Rev. B* 23, 6503 (1981).

⁴D. A. Huckaby, *J. Chem. Phys.* 54, 2910 (1971).

⁵P. Dean, *Proc. Cambridge Philos. Soc.* 59, 383 (1963).

⁶W. G. Hoover, A. C. Hindmarsh, and B. L. Holian, *J. Chem. Phys.* 57, 1980 (1972).

⁷W. T. Ashurst and W. G. Hoover, *Phys. Rev. B* 14, 1465 (1976).

⁸H. S. Carman and D. A. Huckaby, *J. Chem. Phys.* 75, 4651 (1981).

⁹R. H. Kincaid and D. A. Huckaby, *J. Chem. Phys.* 76, 3836 (1982).