Acoustic crystal thermodynamic integration method

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The acoustic crystal thermodynamic integration method is a generalization of the Einstein crystal method developed by Frenkel and Ladd. The name is derived from the acoustic branches of the phonon spectrum of the reference system. The method is designed to calculate the Helmholtz free energy of classical solid phases using Monte Carlo or molecular dynamics simulations. It has several advantages over the Einstein crystal method. For large systems, the Einstein crystal method suffers from very long correlation times near the zero coupling limit because the reference system breaks the overall translational symmetry of model systems. The acoustic crystal method does not break translational symmetry, so correlation times for the acoustic crystal are small. This makes the acoustic crystal method superior to the Einstein crystal method for large system sizes. Also the acoustic crystal method does not artificially introduce long-range order in low-dimensional systems.

I. INTRODUCTION

Monte Carlo [1] and molecular dynamics [2] simulation methods are widely used to calculate thermodynamic properties of the solid and liquid phases of model systems of interacting particles. These methods are very useful for determining the properties of the liquid and solid phases of models but, because of hysteresis, are not particularly well suited for determining the location and properties of the melting transition. The location of a first-order melting line can be determined using Maxwell's double tangent construction if the free energy densities of the solid and liquid phases are both known. Simulation methods at a single point in the phase diagram such as variants of the Widom particle insertion method [2] can determine the free energy at that point, but they are generally not useful in high density solid phases because of the extremely low probability of successful particle insertion. The alternative is to use a sequence of simulations to determine the free energy difference between any point in the phase diagram of the model system and the known free energy of a reference system. The free energy difference is given by a thermodynamic integration along a reversible path between the model system and the reference system. This paper describes a method for calculating the free energy of solid phases in classical statistical mechanics by a thermodynamic integration to a reference system whose particles are harmonically coupled to their nearby neighbors. This method is a generalization of the Einstein crystal method developed by Frenkel and Ladd [2–4]. Like Frenkel and Ladd's method, this method works for both hard and soft interaction potentials. Other thermodynamic integration methods [2,5] work well for soft potentials.

The acoustic crystal thermodynamic integration method has several advantages over the Einstein crystal method.

(1) The acoustic crystal Hamiltonian is invariant to a uniform translation of the entire system. The Einstein crystal method breaks the overall translational symmetry.

(2) The breaking of translational symmetry in the Einstein crystal method imposes long-range translational order on the system for all nonzero couplings. This is important in low dimensions ($d \leq 2$) where model systems do not display long-range translational order [6]. Because of this, the thermodynamic integration integrand in the Einstein crystal method is divergent in the thermodynamic limit at zero coupling. Therefore many points are needed near the zero coupling limit to calculate the integral accurately.

(3) The Einstein crystal method requires the use of an ensemble in which the center of mass of the system is fixed in order to deal with the translational symmetry breaking that occurs for nonzero coupling. This does not add significantly to the complexity of a calculation, but it is not necessary in the acoustic crystal method.

(4) The Einstein crystal method suffers from long Monte Carlo correlation times (of order L^2 where L is the linear dimension of the crystal) at small coupling. While the center-of-mass ensemble effectively deals with the zero wave-vector modes, many long wavelength (small wave-vector) modes remain. The difference between the Einstein crystal method and the acoustic crystal method is due to differences in the classical phonon spectra of the reference systems. The spectrum of the Einstein crystal has frequencies $\omega_{k,s}$ that are independent of wave vector, whereas the spectrum of the acoustic crystal consists of acoustic branches that vanish linearly as wave vector $k \to 0$. For small coupling, the small wave-vector modes of the model system evolve slowly due to correlated diffusive motion on length scales of order $1/k$. This results in energy-energy correlation times of order L^2 at small coupling. By contrast, the acoustic crystal correlation time is independent of L at small coupling because the contribution to the energy of those modes vanishes as $k \to 0$.

One disadvantage of the acoustic crystal method compared to the Einstein crystal method is the added complexity of calculating the acoustic crystal harmonic energy compared to the simpler Einstein crystal energy. This extra effort is justified for large systems because of the increased accuracy attainable in the acoustic crystal method due the smaller correlation times. The acoustic crystal method also requires one to diagonalize the dynamical matrix to determine the free energy of the reference system at large coupling. The dy-

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namical matrix diagonalization for the Einstein crystal is trivial. The calculation of the acoustic crystal phonon frequencies is straightforward if the reference system has crystalline order. Otherwise, the method requires one complete numerical eigenvalue decomposition of the $Nd \times Nd$ dynamical matrix.

II. METHOD

The goal of the acoustic crystal method is to determine the Helmholtz free energy of the solid phase of a model system using a sequence of Monte Carlo or molecular dynamics simulations. The reduced configurational free energy per particle of N particles in volume V is

$$f = -\frac{1}{N}\ln\left(\frac{Q_N}{\sigma^{Nd}}\right) = \frac{F_N(T,V)}{Nk_BT} - d\ln\left(\frac{\Lambda(T)}{\sigma}\right), \quad (1)$$

where $F_N(T,V)$ is the Helmholtz free energy, $\Lambda(T)$ is the thermal de Broglie wavelength,

$$Q_N = \frac{1}{N!}\int \exp[-\beta U_0(\vec{r}_1, \vec{r}_2, \ldots, \vec{r}_N)]d^N\vec{r} \quad (2)$$

is the configurational partition function, $\beta = 1/(k_BT)$ is the inverse temperature, σ is an arbitrary length scale, and d is the dimension. The particle interactions of the model system contained in the potential energy $U_0(\vec{r}_1, \vec{r}_2, \ldots, \vec{r}_N)$ are assumed to be invariant to a uniform translation of all N particles. In the acoustic crystal method one adds a term to the particle interaction energy proportional to a dimensionless coupling constant λ,

$$\beta U = \beta U_0 + \lambda\beta U_1, \quad (3)$$

where, for example,

$$U_1 = \frac{m\omega_0^2}{4}\sum_{\vec{R}}\sum_{\vec{\delta}}\{\hat{\delta}\cdot[\vec{r}(\vec{R}+\vec{\delta}) - \vec{r}(\vec{R}) - \vec{\delta})]\}^2. \quad (4)$$

The total interaction energy of the system is U, and U_1 is the acoustic crystal energy. The sums in Eq. (4) are over all lattice points $\vec{R}$ and all nearest neighbor vectors $\vec{\delta}$ and corresponding unit vectors $\hat{\delta}$. An extra factor of 1/2 in Eq. (4) accounts for double counting of the quadratic couplings. In the limit $\lambda \to 0$, the model system is recovered. This potential energy is the quadratic order approximation of a set of springs with spring constant $m\omega_0^2$ and length of one lattice spacing that couple nearest neighbor particles on the lattice. We have chosen a specific quadratic form for the harmonic coupling but almost any quadratic coupling that has the same crystalline symmetry as the model solid phase and preserves the overall translational invariance will work. The Einstein crystal energy has the simpler form

$$U_1 = \frac{m\omega_0^2}{4}\sum_{\vec{R}}[\vec{r}(\vec{R}) - \vec{R}]^2. \quad (5)$$

The key difference compared to the acoustic crystal is that the normal modes of the Einstein crystal dynamical matrix form d degenerate optical mode branches with frequency ω_0 independent of wave vector. The acoustic crystal has d acoustic mode branches that vanish at the center of the Brillouin zone.

The configurational partition function of the solid phase of the acoustic crystal with coupling λ is given by

$$Q_N(\lambda) = \int \exp(-\beta U_0 - \lambda\beta U_1)d^N\vec{r}. \quad (6)$$

The $N!$ factor has been removed because of the specific choice of the crystalline configuration of the particles. The reduced configurational free energy per particle is given by

$$f(\lambda) = -\frac{1}{N}\ln\left(\frac{Q_N(\lambda)}{\sigma^{Nd}}\right). \quad (7)$$

The free energy of the model system at $\lambda = 0$ is determined by a thermodynamic integration from $\lambda = 0$ to $\lambda = \lambda_0$, where λ_0 is chosen large enough that the model system's interactions are negligible or can be treated perturbatively. There is an implicit assumption that the path between the model system and the reference system is reversible. The free energy of the model system $f = f(0)$ is given by

$$f = f(\lambda_0) - \int_0^{\lambda_0}\frac{\partial f}{\partial\lambda}d\lambda = f(\lambda_0) - \int_0^{\lambda_0}u(\lambda)d\lambda, \quad (8)$$

where $u(\lambda) = \langle\beta U_1\rangle_\lambda/N$ is the average harmonic energy per particle at coupling λ scaled by k_BT. If the free energy at λ_0 is known exactly, or can be determined perturbatively from a simulation at that value of the coupling, then the free energy of the model system can be determined from Eq. (8). The integral can be evaluated by calculating the average acoustic crystal energy from simulations at enough intermediate values of λ to accurately approximate the integral (8) by a sum. For hard potentials in which the pair interactions vanish when particles are not in contact, one can simply choose the limiting coupling λ_0 to be large enough so that the hard collisions are extremely infrequent. One may include the hard interactions perturbatively [2,3] but this is not really necessary if λ_0 is chosen large enough. Typically $\lambda_0 \approx 10^4 - 10^5$ is large enough to ensure that the hard interactions are negligible. Since the equipartition theorem gives $\lambda u(\lambda) \to d/2$ for large λ and the range of integration is over such a large range of coupling, it is convenient to break the integral into two parts:

$$\int_0^{\lambda_0}u(\lambda)d\lambda = \int_0^{\lambda_1}u(\lambda)d\lambda + \int_{\ln(\lambda_1)}^{\ln(\lambda_0)}\lambda u(\lambda)d[\ln(\lambda)]. \quad (9)$$

Each of the integrals can be evaluated by sampling the integrand at points in the interval and by summing, using any standard numerical integration method. We used evenly spaced points and Simpson's rule. The intermediate point was chosen as $\lambda_1 = 1$ and the spacing in the second integral

was $\lambda_j = b^j$, where $b = \sqrt{2}$. This was sufficiently fine to ensure that uncertainties are dominantly due to the statistical uncertainties in the integrand rather than errors introduced by the numerical integration itself.

The partition function of the acoustic crystal in the large coupling limit in d dimensions can be determined from the normal modes of the Nd-dimensional dynamical matrix (see Appendix A):

$$Q_N^{AC}(\lambda) = \frac{V}{N} N^{d/2} \prod_{k \neq 0, s} \sqrt{\frac{2\pi}{\lambda \beta m \omega_{k,s}^2}}. \tag{10}$$

The eigenvalues are labeled by N values of k and d values of s that label the d different phonon polarizations. Since the couplings preserve the translational symmetry of the model system, there are always exactly d zero eigenvalues. For couplings that form a periodic lattice, the eigenvalues of the dynamical matrix can be determined by diagonalizing the dynamical matrix in the Fourier space [7]. See Appendix B. In that case the label k refers to the N k-space points in the Brillouin zone. The acoustic crystal reference system reduced configurational free energy per particle (7) is then

$$f_{AC}(\lambda_0) = \frac{1}{2N} \sum_{k \neq 0, s} \ln(\beta m \omega_{k,s}^2 \sigma^2) + \frac{d(N-1)}{2N} \ln\left(\frac{\lambda_0}{2\pi}\right)$$

$$- \frac{d}{2N} \ln(N) - \frac{1}{N} \ln\left(\frac{V}{N\sigma^d}\right). \tag{11}$$

The Einstein crystal free energy (with fixed center of mass and a final space integration over the center-of-mass location) is a special case of equations (10) and (11). The Einstein crystal has all eigenvalues $\omega_{k,s} = \omega_0$. References [2] and [3] have an incorrect N dependence of the partition function (10) and the free energy (11) that is evident for small N, but this has been corrected in Ref. [4].

III. EXACT TESTS

A one-dimensional system of hard beads on a ring is exactly integrable. The partition function for N identical hard beads of diameter σ on a ring of length $L = Na$ is given by

$$Q_N^{Hard\ Bead} = \frac{1}{N} \int_0^{Na} dx_1 \int_{x_1 + \sigma}^{Na + x_1 - (N-1)\sigma} dx_2 \ldots$$

$$\times \int_{x_{N-1} + \sigma}^{Na + x_1 - \sigma} dx_N$$

$$= \frac{N^N}{N!} a(a - \sigma)^{N-1}. \tag{12}$$

The parameter a represents the average "lattice" spacing on the ring. Equation (12) is easily derived from Tonks' [8] result by fixing the first (or the last) particle on the ring of length L and then integrating over the possible locations of that particle, accounting for indistinguishability. A system of hard rods in one dimension does not form a long-range ordered lattice, but both the Einstein crystal method and the
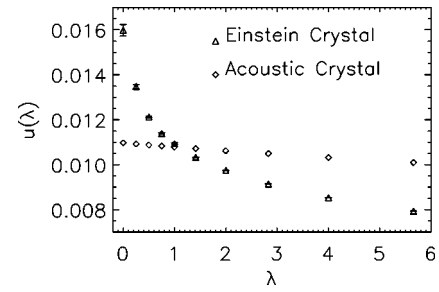

FIG. 1. The small λ harmonic energy vs coupling for systems of 256×256 hard disks in two dimensions for $a = 1.10\sigma$. Both axes are dimensionless. Note the logarithmic singularity of the energy and the large uncertainties at small coupling for the Einstein crystal. The singularity is due to the lack of long-range order and the large uncertainties are due to the long correlation times. The error bars for the acoustic crystal are invisible on this scale.

acoustic crystal method can be used to calculate the free energy of the model for finite N. Extensive tests for small N verify the aptness of the method. The acoustic crystal method continues to work even for very large systems ($N > 1000$), whereas the accuracy of the Einstein crystal method begins to suffer from the effects described in the following section for large $N > 100$.

One can also test the Einstein crystal method and the acoustic crystal method in two dimensions by numerically determining the four particle partition function by using a standard Monte Carlo integration [10]. The eight-dimensional integral

$$Q_4^{Hard\ Disks} = \frac{1}{4!} \int d\vec{r}_1 \int d\vec{r}_2 \int d\vec{r}_3 \int d\vec{r}_4$$

$$\times \exp[-\beta U(\vec{r}_1, \vec{r}_2, \vec{r}_3, \vec{r}_4)] \tag{13}$$

is easily determined by randomly choosing particle positions in a periodic volume of four primitive cells and checking for overlaps. A system of four hard disks with diameter σ and nearest neighbor lattice spacing of $a = 1.10\sigma$ has a free energy $f_4 = -\ln(Q_4/\sigma^8)/4 = 2.431 \pm 0.005$. Both the Einstein crystal and acoustic crystal methods agree with this result.

IV. TEMPORAL CORRELATIONS

The acoustic crystal method is substantially more accurate than the Einstein crystal method for systems larger than about 100 lattice spacings on a side. The accuracy of the Einstein crystal method is degraded by two effects: the integrand $u(\lambda)$ is divergent as $\lambda \to 0$ in the thermodynamic limit for dimensions $d \leq 2$ and, more importantly, the Einstein crystal energy-energy correlation time is divergent in the thermodynamic limit as $\lambda \to 0$ for all $d < 4$.

The former is caused by the lack of long-range order for model systems in $d \leq 2$ [6]. The Einstein crystal coupling imposes long-range order whether the model system has it or not. For model systems in one dimension $\langle u_{R,\alpha}^2 \rangle \sim N$. In two dimensions $\langle u_{R,\alpha}^2 \rangle \sim \ln(N)$. This makes $u(\lambda)$ a singular function of λ at small λ so many points at small λ are necessary

to accurately determine the integral in Eq. (9). See Fig. 1. The acoustic crystal method does not have this shortcoming, because it exhibits short-range order in one dimension and quasi-long-range order in two dimensions like a typical model system. The acoustic crystal interactions smoothly change the spatial correlations of the model system as a function of λ rather than abruptly creating long-range order for $\lambda \neq 0$.

The more important effect is the long correlation times that occur in the Einstein crystal. These result from a Brillouin zone center singularity in the harmonic energy-energy correlation function $\phi(t)$ defined by [9]

$$\phi(t) = \frac{\langle u(t)u(0) \rangle - \langle u(t) \rangle \langle u(0) \rangle}{\langle u^2 \rangle - \langle u \rangle^2}. \tag{14}$$

The dimensionless "time" t is measured in Monte Carlo steps per particle (MCS). The effective number of statistically independent configurations is

$$N_{eff} = \frac{N_{MCS}}{2\tau + 1}, \tag{15}$$

where N_{MCS} is the number of MCS used in the simulation and the correlation time τ is defined by

$$2\tau + 1 = \sum_{t=-\infty}^{\infty} \phi(t). \tag{16}$$

Long correlation times degrade the statistical uncertainties of Monte Carlo simulations. Long correlation times occur in the Einstein crystal method near zero coupling for all dimensions $d \leq 4$. In contrast, the correlation time is asymptotically independent of the system size in the acoustic crystal method. The source of this effect is made evident by writing the Einstein crystal energy and acoustic crystal energy using their normal mode expansions:

$$U_1 = \frac{m}{2} \sum_{k,s} \omega_{k,s}^2 \hat{u}_{k,s}^2. \tag{17}$$

In the small coupling limit the evolution of the k-space modes near the zone center is slow because of the long-wavelength hydrodynamic evolution of the normal mode amplitudes $\hat{u}_{k,s}(t)$. The evolution of these modes is governed by the elastic restoring force that acts on spontaneous fluctuations, and the dissipative dynamics of the Monte Carlo method. (Molecular dynamics simulations will exhibit inertial behavior at short time, but the long-time scale dependence will be similar to the MC results.) Even systems defined by hard potentials exhibit elastic behavior [6,11,12]. We are interested in the limit where the Einstein (or acoustic) couplings are negligibly small so the restoring forces are determined by the equilibrium elastic behavior of the model system. Since the model system is in a solid phase and the system is invariant to uniform translations of the whole system, the restoring force acting on the normal mode amplitudes is $-mc_s^2 k^2 \hat{u}_{k,s}(t)$, where c_s represents the long-wavelength longitudinal and transverse sound speeds [14].

The Monte Carlo dynamics of the evolution of these modes is approximately governed by "model B" Langevin dynamics [13,14]

$$\frac{\partial \hat{u}_{k,s}(t)}{\partial t} = -\gamma mc_s^2 k^2 \hat{u}_{k,s}(t) + \eta_{k,s}(t), \tag{18}$$

where $\eta_{k,s}(t)$ is an uncorrelated Gaussian random force and γ is a rate constant determined by the details of the Monte Carlo method. The solution of the normal mode-normal mode correlation function is [13,14]

$$\langle \hat{u}_{k,s}(t) \hat{u}_{k',s'}(t') \rangle = \frac{2k_B T}{mc_s^2 k^2} \delta_{k,k'} \delta_{s,s'} \exp(-\gamma mc_s^2 k^2 |t - t'|). \tag{19}$$

The harmonic energy-energy correlation function Eq. (14) can then be evaluated using Eq. (19):

$$\phi(t) = \frac{\displaystyle\sum_{k,s} \frac{\omega_{k,s}^4}{k^4} \exp(-2\gamma mc_s^2 k^2 |t|)}{\displaystyle\sum_{k,s} \frac{\omega_{k,s}^4}{k^4}}. \tag{20}$$

The sums can be approximated by integrals in a Debye model-like scheme [7] as long as care is taken to handle the small wave-vector singularities. The correlation function (14) should then scale with time at long time as

$$\phi(t) \sim \frac{\displaystyle\int_{(\Lambda a)/L}^{\Lambda} \frac{\omega_{k,s}^4}{k^4} \exp(-2\gamma mc^2 k^2 |t|) k^{d-1} dk}{\displaystyle\int_{(\Lambda a)/L}^{\Lambda} \frac{\omega_{k,s}^4}{k^4} k^{d-1} dk}. \tag{21}$$

The upper limit cutoff Λ (the "Debye wave vector") is set by the size of the Brillouin zone. The lower limit is set by the k-space point spacing near the zone center. The parameter c is a spatially weighted average of the longitudinal and transverse sound speeds as in the Debye model. Equation (21) can be approximately evaluated in the long-time limit. The Einstein crystal correlation function $\phi_{Einstein}(t)$ in less than four dimensions will scale as

$$\phi_{Einstein}(t) \sim \exp(-2\gamma mc^2 |t|/L^2) \tag{22}$$

because of the zone center singularity. Therefore the correlation time is

$$\tau = L^2/(2\gamma mc^2). \tag{23}$$

Note that the zone center singularity is eliminated in the acoustic crystal because $\omega_{k,s} \sim k$ at a small wave vector. Therefore the acoustic crystal correlation time is independent of the system size in all dimensions

$$\phi_{acoustic}(t) \sim \exp(-2\gamma mc^2 |t| \Lambda^2). \tag{24}$$

TABLE I. The reduced configurational free energy per particle f for hard spheres in $d=3$ dimensions and hard disks in $d=2$ dimensions determined using the acoustic crystal method. The parameter L/a is the number of particles along one side of the periodic crystal (triangular in 2D and fcc in 3D), N is the number of particles, a/σ is the ratio of the primitive lattice vector to the particle diameter, η is the packing fraction, f is the reduced free energy, and Δf is the uncertainty in f.

d	L/a	N	a/σ	η	f	Δf
3	∞	∞	1.08	0.5878	5.91196	0.00030
3	∞	∞	1.09	0.5718	5.53618	0.00016
3	∞	∞	1.10	0.5563	5.19631	0.00031
3	12	1728	1.10756	0.5450	4.95469	0.00053
3	16	4096	1.10756	0.5450	4.95647	0.00033
3	24	13824	1.10756	0.5450	4.95841	0.00018
3	∞	∞	1.10756	0.5450	4.95881	0.00016
3	∞	∞	1.11	0.5410	4.88460	0.00032
2	∞	∞	1.01	0.8890	7.91354	0.00026
2	∞	∞	1.02	0.8717	6.51895	0.00029
2	∞	∞	1.03	0.8548	5.69855	0.00024
2	∞	∞	1.04	0.8385	5.11460	0.00023
2	∞	∞	1.05	0.8226	4.65939	0.00024
2	∞	∞	1.06	0.8071	4.28540	0.00025
2	∞	∞	1.07	0.7921	3.96764	0.00025
2	∞	∞	1.08	0.7775	3.69084	0.00010
2	∞	∞	1.09	0.7633	3.44504	0.00022
2	2	4	1.10	0.7495	2.433	0.003
2	16	256	1.10	0.7495	3.21026	0.00095
2	32	1024	1.10	0.7495	3.22056	0.00049
2	64	4096	1.10	0.7495	3.22261	0.00025
2	128	16384	1.10	0.7495	3.22322	0.00012
2	256	65536	1.10	0.7495	3.22328	0.00006
2	∞	∞	1.10	0.7495	3.22335	0.00005

V. HARD DISK AND HARD SPHERE RESULTS

We apply the acoustic crystal thermodynamic integration method to systems of hard disks in two dimensions and hard spheres in three dimensions. The results are shown in Table I. For the largest three-dimensional system ($24\times24\times24$) the small coupling correlation times of the three-dimensional
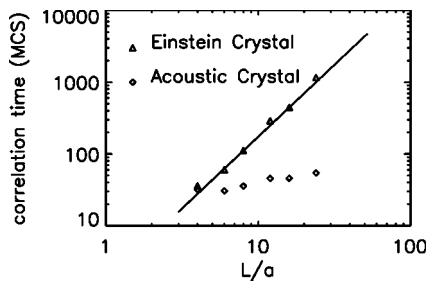

FIG. 2. The Einstein crystal and acoustic crystal correlation times of hard spheres ($\lambda=0$) in three dimensions as a function of system size for $a=1.10\sigma$. Both axes are dimensionless. The line proportional to L^2 shows the theoretical scaling of the Einstein crystal correlation time with system size [Eq. (23)].
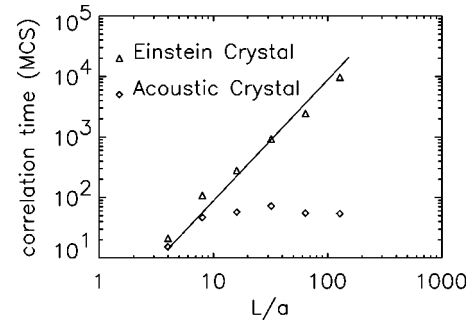

FIG. 3. The Einstein crystal and acoustic crystal correlation times of hard disks ($\lambda=0$) in two dimensions as a function of system size for $a=1.10\sigma$. Both axes are dimensionless. The line proportional to L^2 shows the theoretical scaling of the Einstein crystal correlation time with system size [Eq. (23)].

face centered cubic (fcc) lattice are about 10^3 MCS for the Einstein crystal method compared to about 50 MCS for the acoustic crystal method. In two dimensions the effect is more pronounced because larger linear dimensions are accessible. Correlation times on the order of 10^4 MCS occur for Einstein crystals of 256×256 particles. See Fig. 2 and 3.

Because of the long correlation times and the logarithmic singularity at zero coupling in two dimensions, the uncertainty in the free energy is dominated by a few points near zero coupling for system sizes greater than about 100×100. See Fig. 4. Since the acoustic crystal method does not suffer from this problem, it is a more efficient method for large systems.

Thermodynamic limit values of the configurational free energy per particle were determined by extrapolating $N\rightarrow\infty$. The leading correction to the free energy is proportional to $1/N$. One might expect correction terms of order $\ln(N)/N$ but those appear to be very small. See Fig. 5. The two-dimensional hard disk thermodynamic limit results are well fit by the crystal equation of state free energy [15,16]:

$$f_{Hard\ Disk}=-\ln\left(\frac{4\left(\frac{a}{\sigma}-1\right)}{n_{cp}\sigma^2}\right)+C_0+C_1\left(\frac{a}{\sigma}-1\right)$$

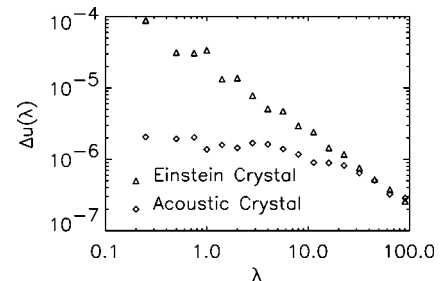$$+c_2\left(\frac{a}{\sigma}-1\right)^2+\ldots. \qquad (25)$$

FIG. 4. The statistical uncertainty of the harmonic energy vs coupling for a 256×256 system of hard disks in two dimensions with $a=1.10\sigma$. Both axes are dimensionless. The large and increasing uncertainty at small coupling for the Einstein crystal is due to the L^2 dependence of the correlation time [Eq. (23)].
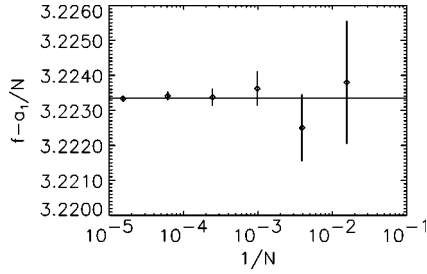
FIG. 5. The finite-size dependence of the two-dimensional hard disk reduced free energy at $a/\sigma = 1.10$. The figure shows the difference between the free energy determined using the acoustic crystal method and the best fit to the form $f(N) = f_\infty + a_1/N$. Both axes are dimensionless. The best fit gives $f(N) = (3.223\,35 \pm 0.000\,05) + (-3.1 \pm 0.1)/N$. The linear dimension of the systems range from $L/a = 8$ to $L/a = 256$ ($N = 64$ to $N = 655\,36$). Any $\ln(N)/N$ corrections that might exist are small.

The ratio of the nearest neighbor lattice spacing to the disk diameter is $a/\sigma = (n_{cp}/n)^{1/d}$, where n is the number density and n_{cp} is the close-packed number density. The best fit to the data over the range $1.01 \leq a/\sigma \leq 1.10$ gives $C_0 = -0.0464 \pm 0.0004$, $C_1 = -0.80 \pm 0.02$, and $C_2 = -1.2 \pm 0.2$. Early work [16] using thermodynamic integration through the solid-liquid phase transition to the ideal gas limit found $C_0 = -0.05 \pm 0.01$ and $C_0 = -0.06 \pm 0.02$. Equation (25) fits the thermodynamic limit acoustic crystal free energy results to within less than 0.001 over the range $1.00 \leq a/\sigma \leq 1.10$.

APPENDIX A

The energy of the acoustic crystal can be written using the dynamical matrix:

$$U_{AC} = \frac{1}{2} \sum_{R,R',\alpha,\alpha'} u_{R,\alpha} D_{\alpha,\alpha'}(R - R') u_{R',\alpha'}, \quad \text{(A1)}$$

The $u_{R,\alpha}$ variables represent particle distances from the equilibrium positions in the d Cartesian directions. The dynamical matrix $D_{\alpha,\alpha'}(R - R')$ has the following properties independent of whether or not the couplings form a periodic lattice.

The $dN \times dN$ dimensional matrix is real and symmetric. The energy is invariant under the translation of all particles by the same vector displacement. The translational invariance implies that d of the eigenvalues vanish. The eigenvectors associated with the zero eigenvalues describe uniform translations of all the particles inside the d-dimensional periodic box that encloses the particles. The couplings are chosen so that all other eigenvalues are positive.

The dynamical matrix for a periodic lattice can be diagonalized in Fourier space and the eigenvectors and eigenvalues indexed using the N k-space points in the Brillouin zone. In the eigenproblem

$$\sum_{R',\alpha'} D_{\alpha,\alpha'}(R - R') \Phi_{R',\alpha'}^{k,s} = m\omega_{k,s}^2 \Phi_{R,\alpha}^{k,s}, \quad \text{(A2)}$$

the eigenvectors $\{\Phi_{R,\alpha}^{k,s}\}$ form a complete orthonormal set. Since the eigenvectors corresponding to the vanishing eigenvalues represent uniform translations, the eigenvectors have the properties

$$\sum_R \Phi_{R,\alpha}^{k \neq 0,s} = 0 \quad \text{(A3)}$$

and

$$\Phi_{R,\alpha}^{k=0,s} = \frac{1}{\sqrt{N}} \delta_{\alpha,s}, \quad \text{(A4)}$$

where $\delta_{\alpha,s}$ is the Kronecker delta. The partition function is

$$Q_N^{AC}(\lambda) = \int \prod_{R,\alpha} du_{R,\alpha} \exp\left(-\frac{\lambda\beta}{2} \sum_{R,\alpha} \sum_{R',\alpha'} u_{R,\alpha} D_{\alpha,\alpha'}(R - R') u_{R',\alpha'}\right). \quad \text{(A5)}$$

We can use the eigenvectors to perform an orthogonal transformation,

$$u_{R,\alpha} = \sum_{k,s} \hat{u}_{k,s} \Phi_{R,\alpha}^{k,s}. \quad \text{(A6)}$$

The partition function can be rewritten in terms of the variables $\hat{u}_{k,s}$.

$$Q_N^{AC}(\lambda) = \int \prod_{k,s} d\hat{u}_{k,s} \exp\left(-\frac{\lambda\beta m}{2} \sum_{k,s} \omega_{k,s}^2 \hat{u}_{k,s}^2\right). \quad \text{(A7)}$$

For large enough λ, one may complete all the Gaussian integrals in Eq. (A7) over the variables associated with the nonzero eigenvalues and make only an exponentially small error:

$$Q_N^{AC}(\lambda) = \left(\int \prod_s d\hat{u}_{0,s} 1\right) \prod_{k \neq 0,s} \sqrt{\frac{2\pi}{\lambda\beta m \omega_{k,s}^2}}. \quad \text{(A8)}$$

The final integral is over the space of allowed values of $\hat{u}_{0,s}$. Due to the translational symmetry, this variable is proportional to the deviation of the center of mass of the particles from the center of mass of the lattice positions:

$$u_\alpha^{cm} = \frac{1}{N} \sum_R u_{R,\alpha} = \frac{1}{N} \sum_R \sum_{k,s} \hat{u}_{k,s} \Phi_{R,\alpha}^{k,s} = \frac{1}{\sqrt{N}} \hat{u}_{0,\alpha}. \quad \text{(A9)}$$

For a crystal of identical particles the center of mass must be confined to one primitive cell of the lattice to avoid over-counting identical configurations. Therefore, the final result for the acoustic crystal partition function is

$$Q_N^{AC}(\lambda) = \frac{V}{N} N^{d/2} \prod_{k \neq 0, s} \sqrt{\frac{2\pi}{\lambda \beta m \omega_{k,s}^2}}. \qquad (A10)$$

This final result also applies to the fixed center-of-mass Einstein crystal [4] in which all the frequency eigenvalues can be chosen to be unity.

APPENDIX B

In one dimension the eigenvalues of the dynamical matrix $\{\omega_k^2\}$ for N particles on a periodic ring coupled by springs with unit spring constant and length of one lattice spacing are

$$\omega_k^2 = 4\omega_0^2 \sin^2\left(\frac{\pi k}{N}\right), \qquad (B1)$$

where $k = 0, 1, \ldots, N-1$.

In two dimensions the eigenvalues of the dynamical matrix $\{\omega_{k,s}^2\}$ for an $N_1 \times N_1$ triangular lattice are given by the eigenvalues of the 2×2 matrices,

$$\omega_0^2 \begin{pmatrix} 4s_1 + s_2 + s_{12} & \sqrt{3}(s_2 - s_{12}) \\ \sqrt{3}(s_2 - s_{12}) & 3(s_2 + s_{12}) \end{pmatrix}, \qquad (B2)$$

where $k_1 = 0, 1, \ldots, N_1 - 1$ and $k_2 = 0, 1, \ldots, N_1 - 1$,

$$s_\alpha = \sin^2\left(\frac{\pi k_\alpha}{N_1}\right) \qquad (B3)$$

and

$$s_{\alpha\beta} = \sin^2\left(\frac{\pi(k_\alpha - k_\beta)}{N_1}\right). \qquad (B4)$$

In three dimensions, the eigenvalues of the dynamical matrix $\{\omega_{k,s}^2\}$ for an $N_1 \times N_1 \times N_1$ face centered cubic lattice are given by the eigenvalues of the 3×3 matrices,

$$\omega_0^2 \begin{pmatrix} 2(s_2 + s_3 + s_{12} + s_{13}) & 2(s_3 - s_{12}) & 2(s_2 - s_{13}) \\ 2(s_3 - s_{12}) & 2(s_1 + s_3 + s_{12} + s_{23}) & 2(s_1 - s_{23}) \\ 2(s_2 - s_{13}) & 2(s_1 - s_{23}) & 2(s_1 + s_2 + s_{13} + s_{23}) \end{pmatrix}, \qquad (B5)$$

where $k_1 = 0, 1, \ldots, N_1 - 1$, $k_2 = 0, 1, \ldots, N_1 - 1$, $k_3 = 0, 1, \ldots, N_1 - 1$ and s_α and $s_{\alpha\beta}$ are defined in Eqs. (B3) and (B4).

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