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Construction and thermodynamic functions of an Einstein crystal with nonlocal interactions

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An assembly of independent oscillators is constructed with the reference length of each oscillator coupled to the total volume of material. Because this coupling is not due to neighbor interactions, the material is referred to as a *nonlocal Einstein crystal*. Closed form thermodynamic functions are derived for both *NVT* and *NPT* ensembles. This crystal can be used as a reference system for thermodynamic integration under finite pressure or tension. It can also be generalized to capture tensorial stress-strain behavior as well as thermal expansion.

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I. INTRODUCTION

The Einstein crystal is one of a handful of systems for which thermodynamic functions can be derived in closed form.[1] In addition to serving as a simple model of solids, the Einstein crystal is often used as a basis from which thermodynamic integration can be carried out to more complex physical systems.[2,3] Since isobaric data is often sought, though, it would be convenient to carry out such integrations at constant pressure. This requires that the basis for integration be a material that has closed form thermodynamic functions but also supports external loads. This paper identifies two existing crystals which satisfy these requirements and offers a new crystal formulation which can also be used.

If the oscillation frequency is made to be a function of volume, then the Einstein crystal can support an external load which allows it to be used as a basis for thermodynamic integration at finite pressures. Within the classical approximation, the Helmholtz free energy of an Einstein crystal in an *NVT* ensemble is given by[4]

$$F = \frac{Nd}{\beta} \ln(\hbar \beta \omega). \tag{1}$$

Here $\beta = 1/(k_b T)$ with k_b as Boltzmann's constant, d is the dimension, ω is the oscillation frequency, and $\hbar$ is the angular form of Planck's constant. The crystal can be endowed with a prescribed pressure response, $\hat{P}(V)$, by solving

$$\left.\frac{\partial F}{\partial V}\right|_{N,T} = -\hat{P}(V)$$

for the required dependence of oscillation frequency, ω, on volume, V:

$$\hat{\omega}(V) = c_1 \exp\left[\frac{-\beta}{Nd}\int dV \hat{P}(V)\right]. \tag{2}$$

Here c_1 is an arbitrary constant of integration. As an example, a pressure response of $\hat{P}(V) = Nd\gamma/\beta V$ calls for a frequency function of $\hat{\omega}(V) = c_1 V^{-\gamma}$, where γ is the Grüneisen parameter.[5,6] Setting the Grüneisen parameter equal to unity gives the pressure response of an ideal gas, and a value of zero removes the pressure dependence of the Einstein crystal entirely.

In addition to the variable frequency Einstein crystal, a harmonic crystal can also be used as a starting point for thermodynamic integration at finite pressures. The *acoustic crystal method* uses a harmonic crystal as a basis for integration at constant volume, but it could be adapted for thermodynamic integration at finite pressures.[7] Unlike the Einstein crystal, though, the harmonic crystal may not be well-suited to assemblies which do not exhibit a uniform lattice structure. For instance, it is not clear how the method would be applied to systems with dislocations, phase interfaces, or grain boundaries.[8]

As an alternative to the Einstein and harmonic crystals, a new crystalline system has been developed which is suitable as a basis for thermodynamic integration at finite pressures. The independent oscillator of the Einstein crystal is replaced by a harmonic sublattice with a size that is coupled to the total volume. It is therefore the static contribution to the potential that depends on volume in contrast to the more standard generalization wherein the oscillation frequency has such a dependence. Because the static coupling is not due to neighbor interactions, the material will be referred to as a *nonlocal Einstein crystal*. In addition to satisfying the requirements for thermodynamic integration under finite pressure and tension, this material offers a basis for considering generalizations which exhibit tensorial stress-strain behavior as well as thermal expansion.

The thermodynamics of this crystal are derived for the *NVT* ensemble and are then rederived for the *NPT* ensemble. The analysis focuses on the development of functions for the Gibbs free energy and the equation of state under both conditions. The *NVT* and *NPT* Gibbs functions are shown to differ, as expected, by terms of order $\ln(N)/N$. The *NPT* functions can then be used to verify isobaric, thermodynamic integration algorithms for small systems.

A one-dimensional, nonlocal Einstein crystal is illustrated in Figs. 1 and 2. For a general, d-dimensional system, each mass is bonded to $2d$ *sublattice points*, and each subsystem represents a single location within the global lattice. The *bond stiffness* is denoted by $k/2d$, and the *sublattice dimension* is $2b$. The distance between the centroids of neighboring sets of the sublattice points is the *global lattice spacing* between oscillators and is denoted by a. The direction of each bond, in the unstrained state, is described by a unit vector, $\hat{n}_j$, with $j \in [1, 2d]$. The vectors point from the centroid of each

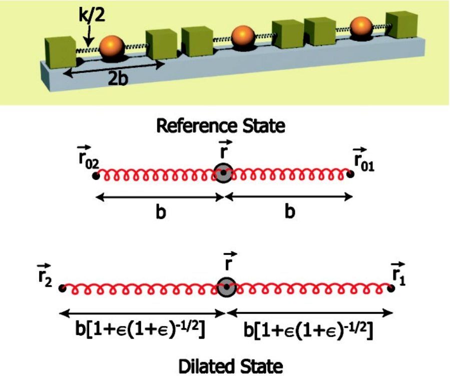

FIG. 1. Schematic of a one-dimensional, nonlocal Einstein crystal.

sublattice to the sublattice points. The equilibrium position of each mass is $\mathbf{r}_{\rm ref}$ while $\mathbf{r}$ gives the instantaneous position. Let the potential energy of one sublattice site be given by

$$\varphi(\mathbf{r};\mathbf{r}_{\rm ref},\epsilon) = \frac{k}{4d}\sum_{j=1}^{2d}\left|\mathbf{r}-(1+\epsilon)^{1/d}\mathbf{r}_{\rm ref}-\frac{b\epsilon\hat{n}_j}{(1+\epsilon)^{1/2}}\right|^2$$
$$= \frac{k}{2}\left(|\mathbf{r}-(1+\epsilon)^{1/d}\mathbf{r}_{\rm ref}|^2+\frac{\epsilon^2 b^2}{1+\epsilon}\right), \qquad (3)$$

where the *global volume strain*, ϵ, is defined as

$$\epsilon = \left(\frac{V}{V_0}\right) - 1 = \left(\frac{\rho_0}{\rho}\right) - 1. \qquad (4)$$

The global lattice spacing between centroids, $a(1+\epsilon)^{1/d}$, implies that the global lattice dilates uniformly in all directions. The size of the sublattice is chosen so that it does not change linearly with the size of the global lattice; the appearance of $1+\epsilon$ in the denominator of the last term in the pair potential precludes the possibility of crystal collapse at high pressures. The bond stiffness, $k/2d$, is taken to be a constant so that the oscillation frequency, $\omega=\sqrt{k/m}$, is constant as well; the dependence of the potential on volume is entirely through the equilibrium length of the oscillator assembly. Note that this potential energy function is harmonic with respect to position but not strain. A pair of bonds is associated with each dimension. Figure 3 portrays a two-dimensional crystal wherein the atoms exhibit cubic symmetry. No symmetry of any sort is required for such crystals though.

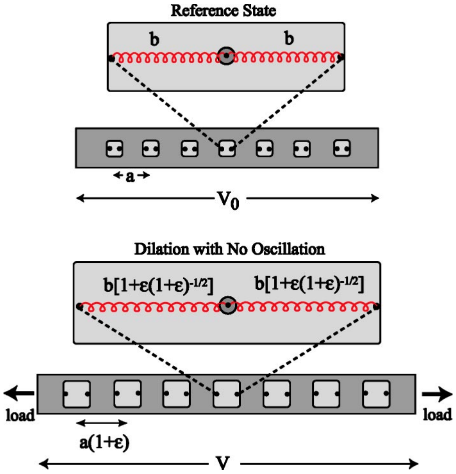

FIG. 2. Dilation of the one-dimensional, nonlocal Einstein crystal.

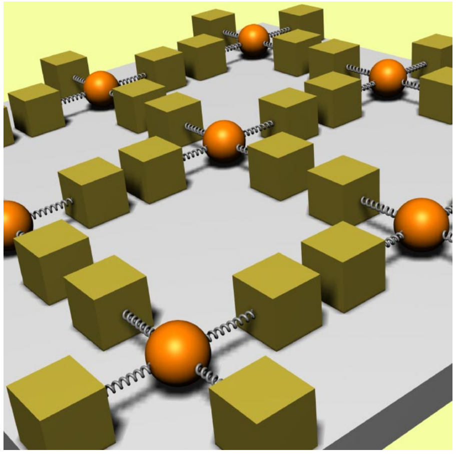

FIG. 3. A two-dimensional *NLE* crystal.

II. *NVT* ASSEMBLIES

A. Thermodynamic relations

For systems governed by a potential $\varphi(\mathbf{r};\mathbf{r}_{\rm ref},\epsilon)$, the configurational part of the Hamiltonian is given by

$$\mathcal{H}_{\rm config}(\underline{\mathbf{r}};\mathbf{r}_{\rm ref},\epsilon) = \sum_{i=1}^{N}\varphi(\mathbf{r}_i;\mathbf{r}_{{\rm ref},i},\epsilon), \qquad (5)$$

with $\underline{\mathbf{r}}:=\{\mathbf{r}_1,\mathbf{r}_2,\ldots,\mathbf{r}_N\}$. Let Z_{NVT} and Q_N be the *NVT partition function* and *NVT configurational partition function*, respectively. Then Q is defined as

$$Q_N(\epsilon) = \frac{1}{N!}\int d\underline{\mathbf{r}}\, e^{-\beta\mathcal{H}_{\rm config}(\underline{\mathbf{r}};\mathbf{r}_{\rm ref},\epsilon)}. \qquad (6)$$

Denote Planck's constant by h and the mass of each oscillator by m. As usual, $\Lambda=\sqrt{\beta h^2/(2\pi m)}$ is the thermal de Broglie wavelength and F is the Helmholtz free energy of the assembly. The following relationships hold:

$$Z_{NVT} = \Lambda^{-dN}Q_N, \quad F = \frac{-1}{\beta}\ln(Z_{NVT}). \qquad (7)$$

A length scale of σ has been adopted in order to render dimensionless the configurational component of the free energy. For instance, if the nonlocal Einstein crystal is to be used as the reference system for thermodynamic integration in hard sphere assemblies, σ is typically taken to be the diameter of one hard sphere.[8] Define the *reduced configurational free energy* of the assembly as

$$f = \frac{\beta F}{N} - d\ln\left(\frac{\Lambda}{\sigma}\right) = \frac{-1}{N}\ln\left(\frac{Q_N}{\sigma^{dN}}\right). \qquad (8)$$

The pressure is given by $P=-(\partial F/\partial V)|_{N,T}$, the Gibbs free

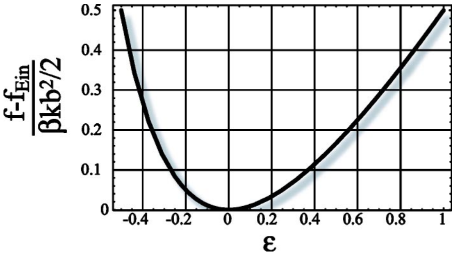

FIG. 4. The excess Helmholtz free energy with respect to the Einstein crystal plotted as a function of volume strain. This result is independent of the system dimension, d. The excess free energy is measured with respect to the classic Einstein crystal.

energy is $G=F+PV$, and the *reduced configurational Gibbs free energy*, g, is defined as

$$g = f + \beta PV/N. \tag{9}$$

Also, with the reduced configurational entropy defined as $s=-(\partial f/\partial T)|_{N,V}$, the *reduced configurational internal energy* u is given by

$$u = f + Ts. \tag{10}$$

Finally, the chemical potential and isothermal bulk modulus are, respectively, $\mu = \partial F/\partial N|_{V,T}$ and $K=-V\,(\partial P \partial V)|_{N,T}$.

B. Thermodynamic functions

The nonlocal Einstein crystal has a configurational partition function, from Eq. (6), of

$$Q_N = \left(\frac{2\pi}{\beta k}\right)^{dN/2} \exp\left[-\frac{\beta N k b^2 \epsilon^2}{2(1+\epsilon)}\right]. \tag{11}$$

The factor of $1/N!$ has been dropped because the oscillators are distinguishable since each is anchored to a set of sublattice points. Note that this reduces to the classic Einstein crystal for the case of no dilation ($\epsilon=0$). Equation (8) then gives the reduced configurational free energy as

$$f = \frac{d}{2}\ln\left(\frac{\beta k \sigma^2}{2\pi}\right) + \frac{\beta k b^2 \epsilon^2}{2(1+\epsilon)} = f_{\mathrm{Ein}} + \frac{\beta k b^2 \epsilon^2}{2(1+\epsilon)}. \tag{12}$$

Here f_{Ein} is the reduced configurational free energy of the classic Einstein crystal. In a manner analogous to that used for comparisons with an ideal gas, define the excess free energy as

$$f_{\mathrm{ex}} = f - f_{\mathrm{Ein}} = \frac{\beta k b^2 \epsilon^2}{2(1+\epsilon)}. \tag{13}$$

This function is plotted in Fig. 4. The equation of pressure for this crystal can be immediately derived from the Helmholtz function:

$$P = -\frac{Nkb^2\epsilon(2+\epsilon)}{2V_0(1+\epsilon)^2} = \frac{Nkb^2}{2V_0}P_{\mathrm{norm}}, \tag{14}$$

where the *normalized pressure* P_{norm} is a function of the strain

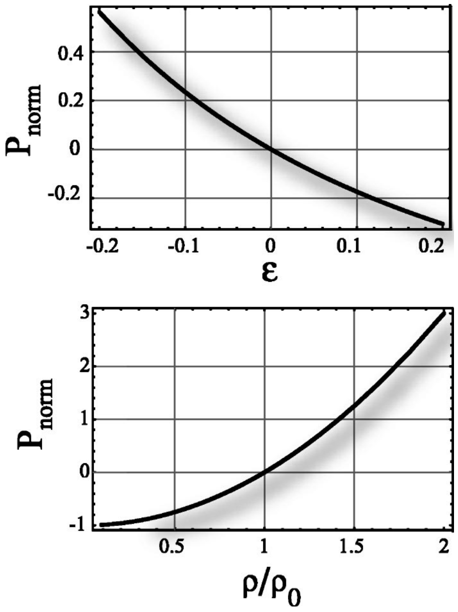

FIG. 5. The equation of pressure for an *NVT* assembly. P_{norm} is defined in Eq. (15) and ρ_0 is the number density at zero strain. The relationship between ρ and ϵ is given in Eq. (4). The plotted results are independent of the system dimension, d.

$$P_{\mathrm{norm}} = \frac{-\epsilon(2+\epsilon)}{(1+\epsilon)^2} = \left(\frac{V_0}{V}\right)^2 - 1. \tag{15}$$

This pressure relation is plotted in Fig. 5.

The reduced configurational internal energy, the reduced configurational Gibbs function, and both the chemical potential and isothermal bulk modulus are

$$u_{NVT} = \frac{d}{2} + \frac{\beta k b^2 \epsilon^2}{2(1+\epsilon)}, \tag{16}$$

$$g_{NVT} = \frac{d}{2}\ln\left(\frac{\beta k \sigma^2}{2\pi}\right) - \frac{\beta k b^2 \epsilon}{1+\epsilon},$$

$$\mu_{NVT} = \frac{d}{2\beta}\ln\left(\frac{\beta k \Lambda^2}{2\pi}\right) + \frac{k b^2 \epsilon^2}{2(1+\epsilon)},$$

$$K_{NVT} = \frac{Nkb^2}{V_0(1+\epsilon)^2}.$$

The entropy and specific heat are identical to that of the Einstein crystal, and all quantities given above reduce to their Einstein crystal counterparts for the special case of zero volume strain.

III. *NPT* ASSEMBLIES

A. Thermodynamic relations

Let Z_{NPT} and Υ_N be the *NPT partition function* and *NPT configurational partition function*, respectively. Then Υ_N is defined as

$$\Upsilon_N = Z_{NPT}\Lambda^{dN} = \frac{1}{V_{\text{char}}}\int d\underline{\mathbf{r}}\, dV e^{-\beta(\mathcal{H}_{\text{config}}+PV)}. \tag{17}$$

The characteristic volume V_{char} is discussed elsewhere and is typically taken to be equal to $1/(\beta P)$.[3,9–13] For the purposes of this investigation, this characteristic volume is left as an undetermined function of pressure, temperature, and number of masses, $V_{\text{char}}(N,P,T)$. Denote Planck's constant by h. The Gibbs free energy is

$$G_{NPT} = \frac{-1}{\beta}\ln(Z_{NPT}) = \frac{-1}{\beta}\ln\left(\frac{\Upsilon_N}{\sigma^{dN}}\right) + \frac{dN}{\beta}\ln\left(\frac{\Lambda}{\sigma}\right).$$

The *reduced configurational Gibbs free energy* for the *NPT* assembly is

$$g_{NPT} = \frac{\beta G_{NPT}}{N} - d\ln\left(\frac{\Lambda}{\sigma}\right) = \frac{-1}{N}\ln\left(\frac{\Upsilon_N}{\sigma^{dN}}\right). \tag{18}$$

The volume is given by $V_{NPT}= \partial G_{NPT}/\partial P|_{N,T}$, the Helmholtz free energy is $F_{NPT}=G_{NPT}-PV_{NPT}$ and the *reduced configurational Helmholtz free energy* f_{NPT} is defined as

$$f_{NPT} = g_{NPT} - \beta PV/N. \tag{19}$$

Also, with the reduced configurational entropy defined as $s_{NPT}=k_b\beta^2\,(\partial_{gNPT}/\partial\beta)|_{N,P}$, the *reduced configurational internal energy*, u_{NPT}, is given by

$$u_{NPT} = g_{NPT} - \frac{\beta PV_{NPT}}{N} + Ts_{NPT}. \tag{20}$$

Finally, the chemical potential and isothermal bulk modulus are, respectively, $\mu_{NPT}= \partial G_{NPT}/\partial N|_{P,T}$ and $K_{NPT}=\frac{-V_{NPT}}{\partial V_{NPT}/\partial P|_{P,T}}$.

B. Thermodynamic functions

The new crystal has a configurational partition function, from Eq. (17), of

$$\Upsilon_N = \left(\frac{2\pi}{\beta k}\right)^{dN/2}\frac{2Nkb^2\beta V_0 e^{\beta Nkb^2}K_1(\Phi)}{V_{\text{char}}\Phi}. \tag{21}$$

Here $K_n(\Phi)$ is the modified Bessel function of the second kind and

$$\Phi = \beta b((bNk)^2 + 2PV_0Nk)^{1/2}. \tag{22}$$

The reduced configurational Gibbs function is then

$$g_{NPT} = \frac{1}{N}\ln\left(\frac{V_{\text{char}}}{V_0}\right) + \frac{d}{2}\ln\left(\frac{\beta k\sigma^2}{2\pi}\right) + \frac{1}{2N}\ln\left(\frac{1}{4}+\frac{PV_0}{2kNb^2}\right) - \beta kb^2 - \frac{1}{N}\ln K_1(\Phi). \tag{23}$$

Because the *NLE* crystal typically has a very large spring stiffness, a small strain assumption is applied in order to simplify the *NPT* thermodynamic functions and to more easily compare them with their *NVT* counterparts. Provided that $\epsilon \ll 1$, Eq. (14) implies that

$$\frac{PV_0}{Nkb^2} = P_{\text{norm}} \ll 1, \tag{24}$$

so that

$$\Phi = \beta kb^2N + \beta PV_0 + \mathcal{O}\left(\frac{PV_0}{Nkb^2}\right)^2 \approx \Phi_{\text{lim}}, \tag{25}$$

$$\Phi_{\text{lim}} = \beta kb^2N + \beta PV_0 \gg 1.$$

Since $\Phi \gg 1$, the following approximation also holds:

$$\ln K_1(\Phi) = -\Phi + \frac{1}{2}\ln\left(\frac{\pi}{2\Phi}\right) + \mathcal{O}\left(\frac{1}{\Phi}\right). \tag{26}$$

Then

$$\frac{-1}{N}\ln K_1(\Phi) \approx +\beta kb^2 + \frac{\beta PV_0}{N} - \frac{1}{2N}\ln\left(\frac{\pi}{2\beta kb^2N + 2\beta PV_0}\right). \tag{27}$$

Substitution into the expression for the free energy gives

$$g_{NPT} \approx \frac{1}{N}\ln\left(\frac{V_{\text{char}}}{bV_0}\right) + \frac{d}{2}\ln\left(\frac{\beta k\sigma^2}{2\pi}\right) + \beta Pv_0 + \frac{3Pv_0}{2kb^2N} - \frac{\beta P^2v_0^2}{2kb^2} + \frac{1}{2N}\ln\left(\frac{\beta kb^2N}{2\pi\sigma^2}\right). \tag{28}$$

This *NPT* Gibbs function can be compared to the *NVT* Gibbs function of Eq. (16) with the latter written as a function of pressure using Eq. (14). The difference between these two function is of order $\ln(N)/N$.

The isobaric equation of state can be derived directly from Eq. (23). Of particular interest is the isobaric equation of pressure:

$$V_{NPT} = \frac{N}{\beta}\frac{\partial g_{NPT}}{\partial P} = \frac{V_0}{\sqrt{1+P_{\text{norm}}}}\frac{K_0(b^2kN\beta\sqrt{1+P_{\text{norm}}})}{K_1(b^2kN\beta\sqrt{1+P_{\text{norm}}})} - \frac{2V_0}{b^2kN\beta P_{\text{norm}}(1+P_{\text{norm}})} + \frac{1}{\beta V_{\text{char}}}\frac{\partial V_{\text{char}}}{\partial P}. \tag{29}$$

Here P_{norm} is defined in Eq. (14). In the interest of direct comparison with the physical volume, the term involving the characteristic volume, V_{char}, is assumed to be negligibly small. Under the approximations of Eqs. (25) and (26), the ratio of Bessel functions have the same value so that

$$V_{NPT} \approx \frac{V_0}{\sqrt{1+P_{\text{norm}}}} = V. \tag{30}$$

This is illustrated in Fig. 6.

Under the approximations of Eqs. (25) and (26), the remaining thermodynamic functions are found to be

$$u_{NPT} \approx \frac{d}{2} + \frac{\beta P^2v_0^2}{2kb^2} - \frac{Pv_0}{Nkb^2}, \tag{31}$$

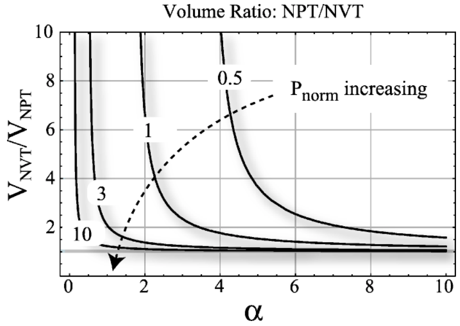

FIG. 6. Ratio of volumes under *NVT* and *NPT* conditions as a function of $\alpha = Nkb^2\beta$. Each curve shown in for a different (normalized) pressure P_{Norm} given by Eq. (15).

$$f_{NPT} \approx \frac{d}{2}\ln\left(\frac{\beta k\sigma^2}{2\pi}\right) + \frac{\beta P^2 v_0^2}{2kb^2} + \frac{Pv_0}{2Nkb^2} + \frac{1}{2N}\ln\left(\frac{\beta kb^2 N}{2\pi\sigma^2}\right) - \frac{1}{N} - \frac{1}{N}\ln(Nv_0),$$

$$\mu_{NPT} \approx \frac{d}{2\beta}\ln\left(\frac{\beta k\Lambda^2}{2\pi}\right) + \frac{1}{2N\beta} - \frac{3Pv_0}{2N\beta kb^2},$$

$$K_{NPT} \approx 2P + \frac{Nkb^2}{V_0}.$$

The reference volume per sublattice site, $v_0 = V_0/N$, is used to more clearly identify the dependence of the thermodynamic functions on the number of particles. In deriving these expressions, terms involving the characteristic volume, V_{char}, were assumed to be negligibly small. These *NPT* functions can be compared to their *NVT* counterparts of Eqs. (12) and (16) by using Eqs. (4) and (14) to rewrite the *NVT* expressions in terms of pressure, P, instead of strain, ϵ. Within the small strain approximation, the difference between pairs of functions is of order $\ln(N)/N$ for the Helmholtz free energy and is zero for the bulk modulii; the difference between pairs is otherwise of order N^{-1}. The entropy and specific heat are identical to that of the Einstein crystal, and all quantities given above reduce to their Einstein crystal counterparts for the special case of zero strain.

IV. CONCLUSIONS

A new crystal has been constructed that has closed form thermodynamic functions and is capable of supporting an external tensile and compressive loads. The independent oscillator of an Einstein crystal is replaced by a harmonic sublattice with a size that is coupled to the total volume. It is therefore the static contribution to the potential that depends on volume in contrast to the more standard generalization wherein the oscillation frequency has such a dependence. Because the static coupling is not due to neighbor interactions, the material is referred to as a *non-local Einstein crystal*. The equation of state was derived for this material under both *NVT* and *NPT* ensembles. Within the small strain approximation, the difference between analogous functions is of order $\ln(N)/N$ for the Helmholtz and Gibbs free energies. The bulk modulus is the same in both ensembles, and the difference between all other pairs of functions is of order N^{-1}.

The nonlocal Einstein crystal can be used as a starting point for thermodynamic integration under constant load. A generalization of the potential would result in a structure that supports shear loads, and using dissimilar bonds within each bonding pair will cause the material to exhibit thermal expansion.

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