

Supplementary information: Free energy calculations for atomic solids through the Einstein crystal/molecule methodology using GROMACS and LAMMPS

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The Helmholtz free energy of a solid can be computed using either the Einstein Crystal [1] or the Einstein molecule method [2]. The two mainly differ for the choice of the reference system: in the Einstein crystal the reference system is an ideal Einstein crystal where the center of mass is kept fixed, whereas in the Einstein molecule the reference system is an ideal Einstein crystal where one particle is kept fixed.

The Helmholtz free energy (A_{sol}) of a solid can be written as the sum of three terms:

$$A_{sol}(T, V) = A_0(T, V) + \Delta A_1(T, V) + \Delta A_2(T, V), \quad (1)$$

where A_0 is the free energy of the ideal Einstein crystal reference system (including corrections for the fixed point), ΔA_1 is the free energy difference between the ideal Einstein crystal and the Einstein crystal in which particles interact through the Hamiltonian of the solid of interest (interacting Einstein crystal) and ΔA_2 is the free energy difference between the interacting Einstein crystal and the solid of interest [3].

A. Analytical calculation of A_0

The analytical calculation of A_0 is different for the Einstein crystal and the Einstein molecule as depends on the chosen reference system. In the Einstein crystal method, A_0 contains the analytical free energy of an ideal Einstein crystal with fixed center-of-mass and the free energy difference between the solid with and without the fixed center-of-mass [3]:

$$\frac{A_0^{EC}}{Nk_B T} = -\frac{1}{N} \ln \left[\frac{1}{\Lambda^{3N}} \left(\frac{\pi}{\beta \Lambda_E} \right)^{3(N-1)/2} N^{3/2} \frac{V}{N} \right] \quad (2)$$

where N is the number of particles, Λ the thermal De Broglie wave length, $\beta = 1/k_B T$ (with k_B the Boltzmann constant), V the system's volume and Λ_E the harmonic spring constant. It can be rewritten as:

$$\frac{A_0^{EC}}{Nk_B T} = \frac{3}{2} \left(1 - \frac{1}{N} \right) \ln \left(\frac{\beta \Lambda_E \Lambda^2}{\pi} \right) + \frac{1}{N} \ln \left(\frac{N \Lambda^3}{V} \right) - \frac{3}{2N} \ln(N) \quad (3)$$

Whereas for the Einstein molecule the expression for A_0 is:

$$\frac{A_0^{EM}}{Nk_B T} = \frac{3}{2} \left(1 - \frac{1}{N} \right) \ln \left(\frac{\beta \Lambda_E \Lambda^2}{\pi} \right) + \frac{1}{N} \ln \left(\frac{N \Lambda^3}{V} \right) \quad (4)$$

The absolute value of A_0 (and therefore of A_{sol}) depends on the value assigned to the thermal de Broglie wave length. However, phase coexistence properties do not depend on this value provided that the same value

of Λ is used in all phases. This just reflects the fact that in classical statistical thermodynamics the values of the masses do not affect coexistence properties. For this reason it is a common practice to set the value of Λ to an arbitrary convenient value. In this work we set the value of the De Broglie thermal wave length (Λ) to σ for the LJ systems and to 1 Å for NaCl. In any case it is always possible to use the correct value of $\Lambda = h/\sqrt{2\pi m k_B T}$ in the calculations.

While A_0 can be computed analytically, numerical simulations are needed to calculate ΔA_1 and ΔA_2 . In this manuscript we show that this calculation can be implemented either with GROMACS or with LAMMPS.

B. Calculation of ΔA_1 with GROMACS/LAMMPS

To compute ΔA_1 , we suggest the following steps both in GROMACS and in LAMMPS:

1. We prepare an ideal Einstein crystal with the crystalline structure of the solid of interest, that means ideal gas particles attached to their lattice positions by harmonic springs.
2. We equilibrate it with GROMACS/LAMMPS fixing either the center-of-mass (Einstein crystal) or the position of one particle (Einstein molecule) while letting all particles (Einstein crystal) or all other particles (Einstein molecule) vibrating through harmonic springs around their lattice positions. Both packages allow to "freeze" either the center-of-mass of the system or one particle's position.
3. The simulation is carried out in the NVT ensemble at the temperature and density of interest, and we recommend to store around $10^4 - 10^5$ configurations of the trajectory to properly compute the ensemble average.

4. ΔA_1 is computed as:

$$\beta \Delta A_1 = \beta U_{lattice} - \ln \langle \exp [-\beta (U_{sol} - U_{lattice})] \rangle_{Ein-id} \quad (5)$$

where $U_{lattice}$ is the potential energy of the perfect lattice, which can be estimated running GROMACS/LAMMPS for a perfect lattice using just one MD step and zero as the time step, and U_{sol} is the potential energy of the instantaneous configuration; evaluated using the intermolecular potential of interest.

Splitting the calculation of ΔA_1 and ΔA_2 allows to choose the proper value for the harmonic spring constant

Λ_E . As an empirical rule, we suggest that a good choice of Λ_E is the one that leads to a value of ΔA_1 approximately $0.02 N k_B T$ higher than the lattice energy $U_{lattice}$. This procedure is important because the latest release of GROMACS does not incorporate yet the Hamiltonian integration, available in the latest release of LAMMPS but only for simple potentials.

C. Calculation of ΔA_2 with GROMACS/LAMMPS

We then evaluate ΔA_2 in a NVT ensemble as

$$\Delta A_2 = - \int_0^{\Lambda_E} \left\langle \sum_i^N (r_i - r_{i,0})^2 \right\rangle_{N,V,T,\Lambda'_E} d\Lambda'_E \quad (6)$$

where the integrand is simply the mean square displacement of each particle from its lattice position. This term can be easily obtained with GROMACS/LAMMPS commands, such as *position-restraint/fix spring/self*, respectively, that apply a spring force on each particle to tether them to their initial position. From the calculation of the total harmonic energy it is possible to compute the mean square displacement for each value of the spring constant (Λ'_E). In fact since $U_{pos-restraint} = \Lambda'_E \left\langle \sum_i^N (r_i - r_{i,0})^2 \right\rangle_{N,V,T,\Lambda'_E} = \frac{k'}{2} \left\langle \sum_i^N (r_i - r_{i,0})^2 \right\rangle_{N,V,T,k'}$, the mean square displacement is simply obtained by dividing $U_{pos-restraint}$ by either Λ'_E or $k'/2$ (notice that $\Lambda'_E = k'/2$). The maximum value of Λ'_E used in the calculations is denoted as Λ_E whereas the maximum value of k' used in the calculations is denoted as k . Notice that depending on the program and algorithm one should use either Λ'_E or k' in the input files. We then compute the integral in Eq.6 using the Gaussian quadrature method with 15 values of Λ'_E for the LJ system and 12 for the NaCl system. When implementing the Einstein molecule with LAMMPS we did not use the fix self spring command but rather prepared the initial configuration with "ghosts" atoms at the lattice positions, tethered to the real atoms via harmonic springs with constant Λ'_E .

D. Details on the implementation of the Einstein crystal and Einstein molecule with GROMACS/LAMMPS

When implementing the Einstein crystal method, we need to simulate the system with fixed center-of-mass and the latest releases of GROMACS and LAMMPS can easily keep fixed the system's center-of-mass. Whereas when implementing the Einstein molecule method, we simulate the system keeping fixed the position of one particle, that can be frozen both in GROMACS and in LAMMPS: this let the center-of-mass freely move, as shown in Fig. 1 for MC and GROMACS.

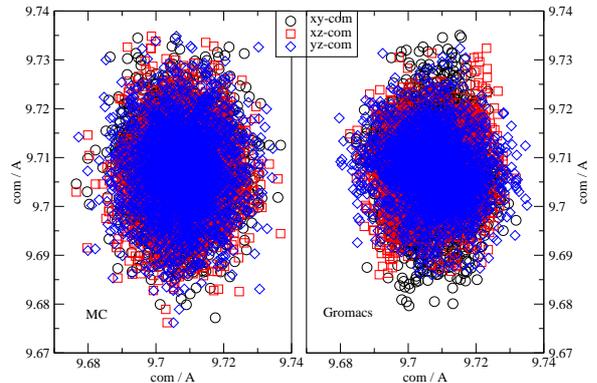


FIG. 1. Center-of-mass displacement of the LJ/STS system for the spring constant $\Lambda'_E = 27.08 k_B T / \text{\AA}^2$ obtained with MC (left-hand side) and GROMACS (right-hand side) obtained in Einstein molecule calculations.

We have simulated Lennard-Jones and JC-NaCl systems in a NVT ensemble using the v-rescaling thermostat[4] and tested that the results obtained do not depend on the chosen relaxation time of the thermostat τ (up to $\tau=2$ ps). In order to show that our results are independent on the chosen thermostat, we have also simulated the LJ/STS using the Langevin thermostat [5] and found no effect on the final calculation of the free energy of the solid. However, we have not equilibrated the system with a Nose-Hoover thermostat [6, 7] since it presents a pathological behavior with harmonic potentials[7].

It is important to choose the time step carefully when computing ΔA_2 or ΔA_1 . The period of an oscillation of an ideal harmonic spring is a function of the spring constant,

$$\frac{1}{\nu} = 2\pi \sqrt{\frac{m}{2\Lambda'_E}} \quad (7)$$

We use a Molecular Dynamics time step of 2.5 - 5.0 fs, since that allowed a correct sampling of the vibrations for the strengths of the springs used in this work.

I. SIMULATION DETAILS

Free energy calculations for the solid were performed in the NVT ensemble. We carry out free energy calculations for a spherically truncated and shifted (STS) and for spherically truncated (ST) LJ systems at $T^* = 2$ and $\rho^* = 1.28$. Free energy calculations were performed for the fcc solid structure. For the STS system we used 256 atoms along with the cutoff distance $r_c = 2.7\sigma$. For the ST system we used 1372 atoms along with the cutoff distance $r_c = 5\sigma$. Simulations results for the LJ potentials (both STS and ST) were implemented using a LJ-Argon system (with $\sigma = 3.405 \text{\AA}$, $\epsilon/k = 120K$ and $m = 39.9$ g/mol). The maximum value of the spring constant was $\Lambda_E = 2500 k_B T / \text{\AA}^2$ for the LJ systems. For NaCl the free energy of the solid was obtained

from NVT runs for a system containing 1000 ions and using the Joung-Cheatham-NaCl model (optimized for SPC/E water). Calculations were performed at 298 K and $V = 24.13 \text{ nm}^3$ (which correspond to the average value of the volume of the system for the considered system size and model obtained from a previous NpT run at 298 K and 1 bar). The maximum value of the spring constant for NaCl was $\Lambda_E = 4000 k_B T / \text{\AA}^2$. For the NaCl system, Ewald sums were used (*Particle Mesh Ewald*, PME [8]) truncating the Coulombic real space contribution and the LJ part of the potential at $r_c = 14 \text{ \AA}$. For convenience we have assigned to both Na and Cl the mass of Ar. Whenever we consider a spherically truncated potential (ST LJ or NaCl), we add the long range corrections to the LJ part of the potential to both energy and pressure. Thus our aim was to estimate the free energy of the untruncated potential rather than of the truncated system itself.

We simulate the systems running NVT Molecular Dynamics for about 10 ns with a time step of 0.0025-0.005 ps (i.e four or two million time steps). For the LJ systems the time step in reduced units is of about $\tau^* = 0.001$, and we have discarded the configurations that corresponds to the first 2 ns of each trajectory. Simulations were carried out in Intel(R) Xeon(R) CPU X5650 @ 2.67GHz processors, which means about 255 ns/day for the 256 LJ atoms system, and 17 ns/day for the 1372 LJ atoms system and the JC-NaCl system. We stored configurations every 100 MD steps, which corresponds to approximately 10^5 independent configurations per simulation run. The temperature was kept constant using the velocity rescale thermostat [4] with a relaxation time of 1 ps.

II. MC VERSUS GROMACS/LAMMPS

To confirm the validity of the free energy calculations obtained with the Molecular Dynamics packages in an NVT ensemble, we simulate the same systems with a NVT Monte Carlo code. For the calculation of ΔA_2 we need to compute the mean square displacement of each particle from its lattice position. Representing the time evolution of the mean square displacement for the LJ/STS computed via MC or GROMACS, we show that both the average and its fluctuations are very similar with the two codes.

It has been shown so far that the free energies ob-

tained from MC and MD agree within their respective error bar. This is true for all the results presented in Table I of the main paper. However, we would like to point out that a somewhat larger deviation (of the order of 0.06 NkT) was observed between MC and MD for a LJ ST system truncated at $r_c = 2.7\sigma$ (data not shown). The deviation is not large but is clearly visible. It is well known that some issues arise when comparing the properties obtained from MC to those obtained from MD for a truncated potential[9, 10]. For instance, if one is interested in the pressure of the truncated potential itself then

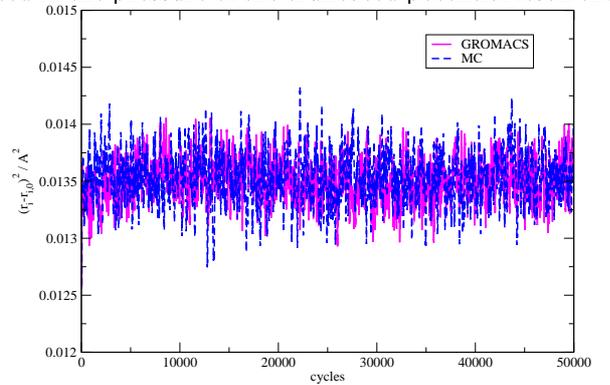


FIG. 2. Mean square displacement of the LJ/STS system for $\Lambda'_E = 27.08 k_B T / \text{\AA}^2$ as obtained with MC and GROMACS from Einstein molecule calculations.

one should add an impulsive correction to the traditional virial expression to evaluate the pressure within a MC NVT run[9, 10]. However a long tail correction is added rather than an impulsive correction in MC runs since one is usually more interested in estimating the properties of the untruncated potential rather than the truncated potential itself. There is no problem in including this long tail correction also in MD runs, and in fact this was done in this work. However the discontinuity of the potential at r_c generates impulsive forces that can not be handled in MD programs as GROMACS/LAMMPS that are based on a Taylor expansion of the particle position. Thus, we recommend to use relatively large system sizes and large cut-off's (above 4.5σ) for the calculation of free energy of solids when using MD to minimize both system size effects and the problem of the discontinuity of the potential at the cutoff.

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