Determining pressure-temperature phase diagrams of materials

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We extend the Nested Sampling algorithm to simulate materials under periodic boundary and constant pressure conditions, and show how it can be efficiently used to determine the phase diagram directly from the potential energy in a highly automated fashion. The only inputs required are the composition and the desired pressure and temperature ranges, in particular solid-solid phase transitions are recovered without any a priori knowledge about the structure of solid phases. We apply the algorithm to the Lennard-Jones system, aluminium, and the NiTi shape memory alloy.

Phase diagrams of materials describe the regions of stability and equilibria of structurally distinct phases and are crucial in both fundamental and industrial materials science. In order to augment experiments, computer simulations and theoretical calculations are often used to provide reference data and describe phase transitions. Although there exist a plethora of methods to determine phase boundaries, such as Gibbs ensemble Monte Carlo,[1] Gibbs–Duhem integration,[2] thermodynamic integration or even direct coexistence simulations, they all require specific expertise and separate setup for each type of phase transition. Moreover, in case of solid phases, where most of the interest lies, advance knowledge of the crystal structure of each phase is required. Methods that systematically explore the potential energy landscape, such as parallel tempering (also known as replica exchange) [3, 4] and Wang-Landau[5], are potential alternatives, but are invariably hampered by convergence problems due to the entropy jump at a first order transition: the probability distributions (parametrised in terms of temperature in case of parallel tempering or energy in case of Wang-Landau) on the two sides of the phase transition have very little overlap resulting in a combination of low acceptance rates and poor exploration.

The Nested Sampling (NS) algorithm[6, 7] was designed to solve this problem. It constructs a sequence of uniform distributions bounded from above by a sequence of decreasing potential energy levels, \( \{E_i\} \), with the property that each level encloses a volume \( \chi_i \) of configuration space that is approximately a constant factor smaller than the volume, \( \chi_{i-1} \), corresponding to the previous level. Hence, each distribution will have an approximately constant fractional overlap with the one immediately before and after, ensuring fast convergence of the sampling and allowing an accurate evaluation of phase space integrals. In particular, the energy level spacings near the phase transition will be very narrow. The sequence of energy levels comprise a discretisation of the cumulative density of states \( \chi(E) \), which allows the evaluation of the partition function at arbitrary temperatures,

\[
Z(N, V, \beta) = \frac{1}{N!} \left( \frac{2\pi m}{\hbar^2} \right)^{3N/2} \int dE e^{-\beta E} \chi'(E) \approx Z_m(N, \beta) \sum_i (\chi_i - \chi_{i-1}) e^{-\beta E_i},
\]

where \( N \) is the number of particles of mass \( m \), \( V \) is the volume, \( \beta \) is the inverse temperature, \( h \) is Planck’s constant, the density of states \( \chi' \) is the derivative of \( \chi \), and we labelled the factor resulting from the momentum integral as \( Z_m \). The total phase space volume is \( \chi_0 = V^N \) corresponding to the ideal gas limit. Note that the sequence of energies and volumes are independent of temperature, so the partition function can be evaluated at any temperature by changing \( \beta \) in [2].

Since its inception Nested Sampling has been used successfully in astrophysics[8], and also to investigate the potential energy landscapes of atomistic systems ranging from clusters to proteins[9–15]. Here we modify the algorithm to allow for a variable unit cell with periodic boundary conditions, thus enabling the determination of constant-pressure heat capacities and hence pressure-temperature phase diagrams of materials directly from the potential energy function without recourse to any other a priori knowledge.

The basic NS algorithm is as follows. We initialise by generating a pool of \( K \) uniformly random configurations and iterate the following loop starting at \( i = 1 \),

1. Record the energy of the sample with the highest energy as \( E_i \), and use it as the new energy limit, \( E_{\text{limit}} \leftarrow E_i \). The corresponding phase space volume is \( \chi_i \approx \chi_0 [K/(K+1)]^i \).

2. Remove the sample with energy \( E_i \) from the pool and generate a new configuration uniformly random in the configuration space, subject to the constraint that its energy is less than \( E_{\text{limit}} \). One way to do this is to clone a randomly chosen existing configuration and make it undergo a random walk of \( L \) steps, subject only to the energy limit constraint.

3. Let \( i \leftarrow i + 1 \), and return to step 1.
At each iteration, the pool of $K$ samples are uniformly distributed in configuration space with energy $E < E_{\text{limit}}$. The finite sample size leads to a statistical error in log $\chi_i$, and also in the computed observables, that is asymptotically proportional to $1/\sqrt{K}$, so any desired accuracy can be achieved by increasing $K$. Note that for any given $K$, the sequence of energies and phase volumes converge exponentially fast (the number of iterations required to obtain results shown below never exceeded 2000 - $K$), and increasing $K$ necessitates a new simulation from scratch. In this, NS is similar to the Wang-Landau method, and in contrast with the case of parallel tempering in which an existing Markov chain can be extended to an arbitrary number of steps to improve convergence.

We now modify the algorithm for the constant pressure case. The integration in (1) needs to be extended over all volumes and all shapes of a periodic unit cell. The partition function describing the system at isotropic pressure to generate a sequence of enthalpies $H_i$, where $H = E(s,V,h_0) + pV$. We split the volume integral into two by imposing an upper limit of $V_0$ (approximating the dilute limit of the ideal gas) on the numerical integration and incorporate the factor $V^{-N}$ into the measure by drawing samples with volumes proportional to $V^{-N}$. Together with the contribution of the tail, corresponding to the ideal gas is, we have

$$
\Delta(N, p, \beta) = Z_m \beta p \int_0^\infty dV V^N \int dh_0 \delta(|h_0| - 1) \times \int ds e^{-\beta(E(s,V,h_0) + pV)},
$$

where $h$ is the $3 \times 3$ matrix of lattice vectors relating the Cartesian positions of the atoms $r$ to the fractional coordinates $s$ via $r = hs$, $V = |h|$ is the volume, and $h_0 = hV^{-1/3}$ is the image of the unit cell normalised to unit volume. NS is performed at fixed pressure to generate a sequence of enthalpies, $H_i$, where $H = E(s,V,h_0) + pV$. We split the volume integral into two by imposing an upper limit of $V_0$ (approximating the dilute limit of the ideal gas) on the numerical integration and incorporate the factor $V^{-N}$ into the measure by drawing samples with volumes proportional to $V^{-N}$. Together with the contribution of the tail, corresponding to the ideal gas is, we have

$$
\Delta(N, p, \beta) = Z_m \beta p \left( \Delta_{\text{NS}}(N, p, \beta, V_0) + \mathcal{O}(1) \times \frac{\Gamma(N + 1, \beta p V_0)}{(\beta p V_0)^N} \right),
$$

where $\Gamma$ is the upper incomplete Gamma function, and the $\mathcal{O}(1)$ factor arises from the integration over lattice shapes as explained in the Supplementary Information, and has no material bearing on the numerical results we report below. The first term is computed using the samples generated by NS, as

$$
\Delta_{\text{NS}}(N, p, \beta, V_0) \approx \frac{V_0^{N+1}}{N+1} \sum_i (\chi_i - \chi_i) e^{-\beta H_i}.
$$
Supplementary Information. Given the partition function, phase transitions can be easily located by finding the peaks of response functions such as the heat capacity, given by

\[ c_p = \left( \frac{\partial H}{\partial T} \right)_p = \left( -\frac{\partial}{\partial T} \right)_p \frac{\partial \ln \Delta(N, p, \beta)}{\partial \beta}. \]  

(6)

By performing separate NS simulations for a range of pressures and combining the pressure and temperature values corresponding to the heat capacity peaks one can straightforwardly construct the entire phase diagram including all thermodynamically stable phases.

To demonstrate the efficacy of NS, we show the phase diagram of the periodic Lennard-Jones model in Figure 1. Most of the phase diagram is accurately recovered using just 64 particles, with finite size errors only apparent for sublimation at low pressures. NS provides a reasonable estimate of the melting and boiling points measured with Bridgman cells, with Diamond anvil cells (DAC) and shock waves (SW) at pressures below the critical point, NS parameters \( K = 800 \) and \( L = 3000 \) were used (the total number of energy evaluations was \( 3 \times 10^6 \)).

FIG. 2. Phase diagrams corresponding to four EAM models of aluminium. Red symbols show the nested sampling results, the error bars are calculated as the width at half maximum of the peaks on the heat capacity curves. On the boiling line points are connected by a solid line up to the critical point. Black symbols show experimental melting points measured with Bridgman cells, with Diamond anvil cells (DAC) and shock waves (SW). Different symbols show the Widom-line, shown by the points with large error bars that correspond to the width of the peak. By performing separate NS simulations for a range of pressures and combining the pressure and temperature values corresponding to the heat capacity peaks one can straightforwardly construct the entire phase diagram including all thermodynamically stable phases.

For our next example we consider aluminium. As one of the most commonly used metals, the thermodynamic properties of aluminium have been extensively studied. The melting line of aluminium has been measured up to 125 GPa, with good agreement between the different experimental techniques, and theoretical calculations were performed using embedded-atom type potentials and \( ab \) initio methods, the latter providing melting temperatures up to 350 GPa. At ambient conditions aluminium crystallises in the face-centred-cubic (fcc) structure, but a phase transition to the hexagonal-close-packed (hcp) structure at 217 GPa has been revealed by X-ray diffraction experiments and the body-centred-cubic (bcc) phase has also been observed in laser-induced microexplosions. The critical points of most metals are not amenable to conventional experimental study and thus estimation of their properties is usually based upon empirical relationships between the critical temperature and other measured thermodynamic properties. In case of aluminium these results in predictions in a wide temperature and pressure range.

We chose four widely used models all based on the embedded-atom method (EAM): (1) the model developed by Liu et al. (LEA-EAM), which is an improved version of the original potential of Ercolessi and Adams, (2) the model developed by Mishin et al. using experimental and \( ab \) initio data as well (Mishin-EAM), (3) the EAM of Mei and Davenport (MD-EAM), and (4) the recently modified version of the MD-EAM, reparametrised by Jasper et al. to accurately reproduce the DFT energies for Al clusters and nanoparticles of various sizes (NPB-EAM).

The phase diagrams for all four models based on NS simulations with 64 particles are shown in Figure 2. The resulting critical parameters vary over a wide range for the different models. Above the critical point, the heat capacity peak corresponding to evaporation does not diminish immediately but broadens gradually resulting in the Widom-line, shown by the points with large error bars that correspond to the width of the peak.

The melting lines are in a good agreement with the available experimental data up to the pressure value \( p \approx \).
25 GPa. Above that the melting curves of the different potentials diverge from the experimental results, except for the MD-EAM potential, which reproduces melting curve remarkably well.

At higher pressures a small peaks appear on the heat capacity curves below the melting temperature for all models, indicating solid-solid phase transitions. We post processed the samples from the NS simulations which revealed that while at low pressures the fcc structure is the most stable for all four models as expected, the models differ markedly in their predictions for high pressure phases, with the only commonality being that their prediction for the upper critical pressure for the stability of the fcc phase is far too low in comparison with experimental and density functional theory.[13][16][17].

Finally, we show preliminary results for a problem of current scientific interest, the NiTi shape memory alloy[13]. The shape memory effect relies on the structural phase transition from the high temperature austenitic phase (cubic B2 structure) to the low temperature martensitic phase[19]. Figure 3 shows the pressure-temperature-composition phase diagram corresponding to a recent EAM model[50]. The NS results for the phase transition temperature are within 50 K of the experimental value, reproduce the trend with compositional change, and predict a decreasing critical temperature with increasing pressure. It is notable that this EAM model seems successful here despite not reproducing the experimentally observed B19’ structure at low temperature.

By inspecting the configurations near the end of the NS simulation, we found that the potential has a number of different low symmetry minima with energies all within a few meV of each other. A more detailed study of NiTi will be presented elsewhere.

In summary, we have extended the Nested Sampling algorithm to allow simulations of periodic systems under constant pressure conditions and demonstrated how it can be used to determine pressure-temperature-composition phase diagrams. In contrast to existing methods for comparing specific phases, NS explores the entire configuration space without requiring any prior knowledge about the structures of different solid phases with the only necessary input being the composition and the desired pressure and temperature ranges. We suggest that this makes it eminently suitable for validating materials models, and in the future could even play a role in the automatic optimisation of empirical models.

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![FIG. 3. NiTi martensitic phase transition as a function of Ni content (at 0.66 GPa) and pressure (at 1:1 composition). The structure (labelled B19′-X) shown for the low temperature phase is similar to the experimentally observed B19′ structure. The NS parameters were K = 1920, L = 10^5 and each data point used 10^13 energy evaluations, and Ni–Ti swap moves were also included in the MC. Experimental results are from [51].](image-url)

1. A. Z. Panagiotopoulos, Mol. Phys. 61, 813 (1987).
2. D. A. Kofke, Mol. Phys. 78, 1331 (1993).
3. R. H. Swendsen and J. S. Wang, Phys. Rev. Lett. 57, 2607 (1986).
4. D. D. Frantz, D. L. Freemann, and J. D. Doll, J. Chem. Phys. 93, 2769 (1990).
5. F. Wang and D. P. Landau, Phys. Rev. Lett. 86, 2050 (2001).
6. J. Skilling, in AIP Conference Proceedings, Vol. 735 (2004) p. 395.
7. J. Skilling, J. of Bayesian Analysis 1, 833 (2006).
8. F. Feroz and M. P. Hobson, Mon. Not. R. Astron. Soc. 384, 449 (2008).
9. L. B. Pártay, A. P. Bartók, and G. Csányi, J. Phys. Chem. B 114, 10502 (2010).
10. L. B. Pártay, A. P. Bartók, and G. Csányi, Phys. Rev. E 89, 022302 (2014).
11. N. S. Burkoff, C. Várnai, S. A. Wells, and D. L. Wild, Biophys. J. 102, 878 (2012).
12. H. Do, J. D. Hirst, and R. J. Wheatley, J. Chem. Phys. 135, 174105 (2011).
13. H. Do, J. D. Hirst, and R. J. Wheatley, J. Chem. Phys. 116, 4535 (2012).
14. H. Do, and R. J. Wheatley, J. Chem. Theory Comput. 9, 165 (2013).
15. S. Martiniani, J. D. Stevenson, D. J. Wales, and D. Frenkel, Phys. Rev. X 4, 031034 (2014).
16. G. J. Martyna, D. J. Tobias, and M. L. Klein, J. Chem. Phys. 101, 4177 (1994).
17. T.-Q. Yu, J. Alejandro, R. López-Rendón, G. J. Martyna, and M. E. Tuckerman, Chem. Phys. 370, 294 (2010).
5

[18] G. C. McNeil-Watson and N. B. Wilding, The Journal of chemical physics 124, 064504 (2006).
[19] D. A. Kofke, The Journal of chemical physics 98, 4149 (1993).
[20] R. Agrawal and D. A. Kofke, Molecular Physics 85, 43 (1995) [http://dx.doi.org/10.1080/0026897950100921].
[21] D. Errandonea, J. App. Phys. 108, 033517 (2010).
[22] R. Boehler and M. Ross, Earth and Planetary Science Letters 153, 1 (1997).
[23] A. Hänström and P. Lazor, Journal of alloys and compounds 305, 209 (2000).
[24] J. W. Shaner, J. M. Brown, and R. G. McQueen, “Melting of metals above 100 gpa,” in High Pressure in Science and Technology, edited by C. Homan, R. K. MacCrone, and E. Whalley (Amsterdam: North-Holland, 1984) pp. 137–141.
[25] A. A. Likalter, Physica A 311, 137 (2002).
[26] V. Fortov and I. Iakubov, Non-Ideal Plasma (Plenum Press, New York, 2000).
[27] D. A. Young and A. B. J, Phys. Rev. A 3, 364 (1971).
[28] P. Renaudin, C. Blanchard, J. Clerouin, G. Faussurier, P. Noiret, and V. Recoules, Phys. Rev. Lett. 91, 75002/1 (2003).
[29] D. Bhatt, A. W. Jasper, N. E. Schultz, J. I. Siepmann, and D. G. Truhlar, J. Phys. Chem. B 109, 3915 (2005).
[30] J.-C. Boettger and S. B. Tricke, Phys. Rev. B 53, 3007 (1996).
[31] G. V. Sinko and N. A. Smirnov, J. Phys.: Condens. Matter 14, 6989 (2002).
[32] W. J. Buehler, J. W. Gilfrich, and R. C. Wiley, J. Appl. Phys. 34, 1475 (1963).
[33] K. Bhattacharya, Why It Forms and How It Gives Rise to the Shape-Memory Effect (Oxford University Press, Oxford, UK, 2003).
[34] Y. Zhong, K. Gall, and T. Zhu, J. App. Phys. 110, 033532 (2011).
[35] J. Frenzel, E. George, A. Dlouhy, C. Somsen, M.-X. Wagner, and G. Eggeler, Acta Materialia 58, 3444 (2010).