Calculation of elastic constants of embedded-atom-model potentials in the NVT ensamble

Menahem Krief and Yinon Ashkenazy
Racah Institute of Physics, The Hebrew University, 9190401 Jerusalem, Israel

A method for the calculation of elastic constants in the NVT ensemble, using molecular dynamics (MD) simulation with a realistic many-body embedded-atom-model (EAM) potential, is studied in detail. It is shown that in such NVT MD simulations, the evaluation of elastic constants is robust and accurate, as it gives the elastic tensor in a single simulation which converges using a small number of time steps and particles. These results highlight the applicability of this method in: (i) the calculation of local elastic constants of non-homogeneous crystalline materials and (ii) in the calibration of interatomic potentials, as a fast and accurate alternative to the common method of explicit deformation, which requires a set of consistent simulations at different conditions. The method is demonstrated for the calculation of the elastic constants of copper in the temperature range of 0-1000K, and results agree with the target values used for the potential calibration. The various contributions to the values of the elastic constants, namely, the Born, stress fluctuation and ideal gas terms, are studied as a function of temperature.

I. INTRODUCTION

The calculation of thermo-elastic properties of materials using computer simulations, plays a key role in understanding the response of materials to deformation under varying conditions. In a wide range of applications, material structure leads to local variation in the elastic response functions, due to grain boundaries and heterophase interfaces. It is this local variation of elastic properties that allow tailoring of the macroscopic effective material properties. The development of a model for the relation between composite material specific local property and an effective average response function depends on understanding how local properties contribute and interact in order to generate an observable average response. Furthermore, local elastic properties are not accessible experimentally for a wide range of systems, and so reliable numerical evaluation of these may play a key role in the development of effective models for composite materials.

While it is well established that various thermal and mechanical properties can be evaluated for various atomistic structures by atomistic simulations, it is also well established that such evaluation requires addressing non pairwise terms. The widely used embedded atom model (EAM)[1], is a fast, simple and accurate method, which allows a correct description of the microscopic interactions in crystalline materials. Molecular dynamics calculations of adiabatic elastic constants (which are performed in the microcanonical NVE ensamble), for metallic elements, using EAM model potentials, were performed in the past [2,3], based on the widely used formulation of Ray et al. [4].

In this manuscript we present and analyze the feasibility, robustness and accuracy of the calculation of elastic constants of metals under constant temperature and volume, that is, in the canonical NVT ensamble. Using the stress-stress formulation [4,6,7], all the components of the elastic constant tensor are obtained in a single molecular dynamics simulation, as opposed to the common explicit deformation method [8,10,11], which requires several simulations under different deformations. In addition, the method allows the evaluation of elastic properties in localized regions within larger non-homogeneous simulation box, unlike first principle methods which allow efficient temperature dependent calculations, but only for a uniform system [17,18]. Finally, it is demonstrated that NVT calculations of elastic constants converge more rapidly in comparison to the NPT strain-strain fluctuations formulation [8,9,10,11], using symplectic numerical integrators [22,23] and Nose-Hoover thermostat chain [28,30].

We performed calculations of the isothermal elastic constants $C_{11}, C_{12}, C_{44}$ of Copper for a widely used realistic tabulated EAM potential by Mishin et al. [31]. This potential successfully reproduces energy and stability of several nonequilibrium configurations as well as transformation paths between different structures. The calculations were compared with experimental results in the temperature range 0-1000K, and a good agreement is achieved. The manuscript is structured as follows: We start with a short review of formalism used from thermoelasticity, then we describe in detail how elastic constants can be calculated using a single MD simulation in the NVT ensamble in Section 3, and conclude with Section 4 in which we employ the described method to calculate elastic constants in Copper for a commonly used EAM potential.

II. THERMOELASTICITY

We start with a brief review of the definitions and notations of thermo-elasticity, that will be used throughout
Kirchhoff stress tensor \[32\], is defined by:

\[ \eta_{\alpha\beta} = \frac{1}{2} \left( \frac{\partial r_{\alpha}}{\partial R_{\alpha}} \frac{\partial r_{\beta}}{\partial R_{\beta}} - \delta_{\alpha\beta} \right), \]

where Greek indices such as \(\alpha, \beta, \gamma\) represent Cartesian components, for which we employ Einstein summation convention. In matrix notation, the strain tensor is related to the Jacobian (metric) tensor:

\[ J_{\alpha\beta} = \frac{\partial r_{\alpha}}{\partial R_{\alpha}}, \]

by:

\[ \eta = \frac{1}{2} \left( J^T J - I \right), \]

where \(I\) is the identity matrix. The difference in dimensions due to deformation can thus be written using the strain tensor \(\eta\) via:

\[ \delta r^2 - \delta R^2 = 2\eta_{\alpha\beta} \delta r_\alpha \delta r_\beta. \]

And the mechanical work due to an infinitesimal deformation with Lagrangian strain \(d\eta_{\alpha\beta}\) is given by \[32\] \[37\]:

\[ \delta W/V_0 = -\tau_{\alpha\beta} d\eta_{\alpha\beta}, \]

where \(V_0\) is the undeformed volume and the thermodynamic tension tensor, also known as the second Piola-Kirchhoff stress tensor \[32\], is defined by:

\[ \tau = \text{det}(J) J^{-1} \sigma J^{-T}, \]

where \(\sigma\) is the Cauchy stress tensor, and the ‘\(-T\)’ superscript denotes matrix transposition and inversion. We note that \(\tau = \sigma\) for a zero applied strain (\(J = I, \eta = 0\)). If the deformation process is reversible (an assumption which excludes plasticity), then the first law of thermodynamics for the internal energy \(E\) is written as:

\[ dE = TdS + V_0 \tau_{\alpha\beta} d\eta_{\alpha\beta}, \]

where \(T\) denotes the temperature and \(S\) the entropy. And changes in the free energy

\[ dF = SdT + V_0 \tau_{\alpha\beta} d\eta_{\alpha\beta}. \]

The thermodynamic tension tensor is the thermodynamic conjugate of the Lagrangian strain tensor:

\[ \tau_{\alpha\beta} = \frac{1}{V_0} D_{\alpha\beta} F, \]

where we used the symmetrical partial derivative operator:

\[ D_{\alpha\beta} = \frac{1}{2} \left( \frac{\partial}{\partial \eta_{\alpha\beta}} + \frac{\partial}{\partial \eta_{\beta\alpha}} \right), \]

due to symmetry of the strain tensor \(d\eta_{\alpha\beta} = d\eta_{\beta\alpha}\) in eq. \[8\]. The Taylor expansion of the elastic free energy around the un-deformed state, \(\eta = 0\), is written as:

\[ F(\eta)/V_0 = F(0)/V_0 + \sigma_{\alpha\beta} \eta_{\alpha\beta} + \frac{1}{2} C_{\alpha\beta\gamma\delta} \eta_{\alpha\beta} \eta_{\gamma\delta} + \ldots \]

\[ (11) \]

where:

\[ \sigma_{\alpha\beta} = \tau_{\alpha\beta}(\eta = 0) = \frac{1}{V_0} D_{\alpha\beta} F \bigg|_{\eta = 0}, \]

\[ (12) \]

and the second order isothermal elastic constants are defined by:

\[ C_{\alpha\beta\gamma\delta} = \frac{1}{V_0} D_{\alpha\beta} D_{\gamma\delta} F \bigg|_{\eta = 0}, \]

\[ (13) \]

where the derivatives in equations \[12\] \[13\] are taken at constant \(T\) and evaluated at zero strain \(\eta = 0\).

III. MOLECULAR DYNAMICS AND ELASTIC CONSTANTS

In this section we briefly outline how the entire isothermal elasticity tensor can be obtained in a single molecular dynamics simulation using the stress-stress fluctuation method \[2\] \[5\] \[8\] \[9\] \[36\] \[38\]. This method is favorable over the widely used explicit deformation method \[8\] \[11\] \[14\], which requires multiple simulations under various deformations, in order to obtain different components of the elasticity tensor.

Starting from the Hamiltonian of a system of \(N\) particles is written as:

\[ H(r^N, p^N) = \sum_i \frac{p_i^2}{2m_i} + V(r_1, ..., r_N), \]

\[ (14) \]

where \(m_i, r^N\) and \(p^N\) denotes, respectively, the masses, position and momentum vectors of the \(N\) particles. The embedded-atom-model (EAM) potential \[1\], is defined by a pair potential \(v = v(r)\), an embedding function \(F = F(\rho)\) and a local electron density function \(\rho = \rho(r)\), so that the potential energy takes the form:

\[ V(r_1, ..., r_N) = \sum_i F(\rho_i) + \sum_{i<j} v(r_{ij}), \]

\[ (15) \]

where \(r_{ij} = r_i - r_j\) is the interatomic vector and the electron density function of particle \(i\) is given by \(\rho_i = \sum_{j \neq i} \rho(r_{ij})\). For an EAM potential of the form \[15\] the force on a particle \(i\) can be written as:

\[ F_i = \sum_{j \neq i} F_{ij} r_{ij}/r_{ij}, \]

\[ (16) \]
where:

\[ F_{ij} = - (v' (r_{ij}) + [F' (\rho_i) + F' (\rho_j)] \rho' (r_{ij})) . \]  

(17)

The instantaneous kinetic temperature is given by:

\[ \frac{1}{2} k_B T_K = \frac{1}{g} \sum_i \frac{p_i^2}{2m_i}, \]  

(18)

where \( k_B \) is Boltzmann’s constant and \( g = 3 (N - 1) \) is the number of degrees of freedom. The instantaneous pressure tensor \( P_{\alpha\beta} \) is obtained from the virial theorem:

\[ P_{\alpha\beta} V = \sum_i \left( \frac{p_{i,\alpha} p_{i,\beta}}{m_i} + r_{i,\alpha} F_{i,\beta} \right). \]

Where \( V \) is the system volume. The total pressure is given by the average of the diagonal components:

\[ P = \frac{1}{3} (P_{11} + P_{22} + P_{33}). \]  

(19)

For an EAM potential, it follows from eq. 16 that:

\[ \sum_i r_{i,\alpha} F_{i,\beta} = \sum_{i<j} F_{ij} \frac{r_{ij,\alpha} r_{ij,\beta}}{r_{ij}}, \]

so that the pressure tensor has the form:

\[ P_{\alpha\beta} V = \sum_i \frac{p_{i,\alpha} p_{i,\beta}}{m_i} + \sum_{i<j} \frac{F_{ij} r_{ij,\alpha} r_{ij,\beta}}{r_{ij}}. \]  

(20)

It can be shown [3, 6, 8, 39, 40], as detailed in Appendix A, that in the NVT ensemble, the elastic constants [13] are given by:

\[ C_{\alpha\beta\gamma\delta} = \langle C_{\alpha\beta\gamma\delta}^B \rangle - \frac{V}{k_B T} \left[ \langle \sigma_{\alpha\beta}^B \sigma_{\gamma\delta}^B \rangle - \langle \sigma_{\alpha\beta}^B \rangle \langle \sigma_{\gamma\delta}^B \rangle \right] + \frac{N k_B T}{V} \langle \delta_{\alpha\gamma} \delta_{\beta\delta} + \delta_{\alpha\delta} \delta_{\beta\gamma} \rangle , \]  

(21)

where \( \langle \cdot \rangle \) represents ensemble average. The last term in eq. 21 is a non configurational ideal gas contribution which vanishes at zero temperature and is related to volume derivatives with respect to the strain tensor. The first term in eq. 21, known as the Born term, is a configurational part which is given by a canonical average of the zero-temperature expression for the elastic constant [3, 8, 41]. The second term in eq. 21 accounts for stress fluctuations and also vanishes at zero temperature (this term is obtained directly from the general identity A11 detailed in Appendix A). The Born stress tensor in eq. 21 is defined by the derivative of the potential energy with respect to strain, evaluated at a state of zero applied strain:

\[ \sigma_{\alpha\beta}^B = \frac{1}{V} D_{\alpha\beta} V \bigg|_{\eta=0}. \]  

(22)

The Cauchy stress tensor is given by:

\[ \sigma_{\alpha\beta} = \langle \sigma_{\alpha\beta}^B \rangle - \frac{k_B T}{V} \delta_{\alpha\beta} \]  

(23)

Similarly, the Born elastic constant term is given by:

\[ C_{\alpha\beta\gamma\delta}^B = \frac{1}{V} D_{\alpha\beta} D_{\gamma\delta} V \bigg|_{\eta=0}. \]  

(24)

For an EAM potential of the form [15] it can be shown that the Born stress has the following form:

\[ V \sigma_{\alpha\beta}^B = - \sum_{i<j} F_{ij} \frac{r_{ij,\alpha} r_{ij,\beta}}{r_{ij}}, \]  

(25)

while the Born elastic constant takes the form [2, 3, 7]:

\[ VC_{\alpha\beta\gamma\delta}^B = \sum_{i<j} X_{ij} \frac{r_{ij,\alpha} r_{ij,\beta} r_{ij,\gamma} r_{ij,\delta}}{r_{ij}^2} \]  

+ \sum_i F'' (\rho_i) g_{i,\alpha\beta} g_{i,\gamma\delta}, \]  

(26)

where:

\[ X_{ij} = v'' (r_{ij}) - \frac{1}{r_{ij}} v' (r_{ij}) \]

+ \( F' (\rho_i) + F' (\rho_j) \left( \rho'' (r_{ij}) - \frac{1}{r_{ij}} \rho' (r_{ij}) \right), \]

(27)

and:

\[ g_{i,\alpha\beta} = \sum_{k \neq i} \rho' (r_{ik}) \frac{r_{ik,\alpha} r_{ik,\beta}}{r_{ik}}. \]  

(28)

For completeness, a detailed derivation of equations 21-28 is given in Appendix A.

IV. RESULTS

Detailed molecular dynamics simulations are performed, in order to demonstrate and analyze the formalism developed in the previous sections, which we employ for the calculation of the elasticity tensor of copper.

The results presented in this work were obtained using a newly developed molecular dynamics code. The computational model employs symplectic numerical integrators, which preserve phase space measures of non-Hamiltonian dynamics [22, 27], incorporates Nose-Hoover thermostat chains in the NVT and NPT ensembles [28, 30], solved using high order Suzuki-Yoshida decomposition [44, 45]. The equations of motions are detailed in appendices B and C for the NVT and NPT ensembles, respectively.

The isothermal elastic constants of Copper were calculated as a function of temperature using a series of molecular dynamics calculations in the NVT ensemble employing a widely used EAM potential by Mishin et al. [31].
This potential is calibrated so that the calculated zero temperature fcc lattice constant is \( L(T = 0) = 3.615\text{Å} \) and the elastic constants are given by \( C_{11} = 169.9\text{GPa}, C_{12} = 122.6\text{GPa} \) and \( C_{44} = 76.2\text{GPa} \) (the Voigt notation will be used throughout this section). In the simulations presented below, a cubical system with 500 atoms was used with their initial positions on an fcc lattice, and with initial velocities sampled from a Maxwell distribution at the appropriate temperature. Periodic boundary conditions were used. The integration of the equations of motion was performed with a time step of \( 26\text{fs} \) for \( 2 \times 10^5 \) steps. A Nose-Hoover thermostat chain of size \( M = 10 \) and a relaxation time of \( \tau_T = 50\text{fs} \) was applied.

The NVT calculations require prior evaluation of the equilibrium volume at zero stress at the various temperatures. These volumes can be evaluated using known thermal expansion coefficient, but we re-evaluated them using a series of zero stress NPT calculations. These yield the lattice constant as a function of temperature, \( L(T) \). The resulting equilibrium thermal expansion ratio, \( L(T)/L(0) - 1 \), is shown as a function of temperature in Fig. 1. An analysis of the thermalization and convergence of a selected NPT simulation at \( T = 300\text{K} \) is presented in detail in figures 2-3. It is evident that convergence is achieved relatively fast with \( 10^4 \text{MD steps} \).

In Fig. 1 the thermal expansion ratio \( L(T)/L(0) - 1 \) of Copper, as a function of temperature, resulting from a series of NPT molecular dynamics simulations at zero pressure in the temperature range 0-1000K. Time dependent measures of the simulation at T=300K are presented in detail in figures 4-9.

In Fig. 1 the isothermal elastic constants as a function of temperature are plotted, together with the contributions of the Born term, the Born stress fluctuation term and the ideal gas kinetic term (see eq. 21). As expected, it is evident that the reduction of the elastic constant with increasing temperature is mainly due to the stress fluctuations term, which is larger at higher temperatures. It is also evident that in the temperature range studied here, the ideal gas contribution is negligible.

Finally, in Fig. 8 we compare the calculated isothermal elastic constants as a function of temperature, with experimental results. In Ref. 42, experimental results for isothermal elastic constants \( C_{11}, C_{12}, C_{44} \) are given in the temperature range 0-300K. In Ref. 43, experimental results for adiabatic elastic constants are given in the range 300-800K. Since the isothermal and adiabatic elastic constants are identical for \( C_{44} \), we can use these experimental results directly. On the other hand, the isothermal and adiabatic elastic constants \( C_{11}, C_{12} \) are not identical [43-45], and were not compared here. It is evident that the agreement between the calculated and experimental values is relatively good, especially given the fact that the Copper potential we used [31] was calibrated to slightly different values at \( T = 0\text{K} \) (the experimental values of Ref. 42 are \( C_{11} = 176.2\text{GPa}, C_{11} = 124.94\text{GPa} \) and \( C_{11} = 81.77\text{GPa} \)). The values that were used to calibrate the tabulated potential (at \( T = 0 \)), are reproduced by our calculations to 5 significant digits. In addition, in Ref. 10 adiabatic elastic constants are calculated by molecular dynamics simulations (using LAMMPS MD code [19]) at \( T = 300\text{K} \), using the same EAM potential and employing the explicit deformation method. This result for \( C_{44} \) is also shown in Fig. 8 showing a very good agreement with our calculation (less than 0.5%).

Results of a specific NVT simulation with \( T = 300\text{K} \) and a volume chosen such that the total pressure is zero, and at results calculated with the same potential (and using LAMMPS [49]). The blue X data point represents the computational \( C_{44} \) result given in Ref. 10.
Figure 2. (Color online) Analysis of a molecular dynamics simulation of Copper in the NPT ensemble at zero pressure and $T = 300K$. The upper left figure shows the instantaneous pressure (eq. 19 red solid line), the cumulative average pressure (black dashed line) and the cumulative pressure standard deviation. The upper middle figure shows the instantaneous kinetic temperature (eq. 15 red solid line, left y-axis), the cumulative average temperature (black dashed line, left y-axis), the relative error between the current cumulative average value to the the final average value (green dotted line) and the ratio between the cumulative standard deviation to the cumulative average (blue solid line, right axis). Similarly, the upper right figure shows the results for the ratio between the simulation box length and the initial box length ($L_0 = 3.165\AA$). The first $2 \times 10^4$ steps are plotted on a logarithmic x scale, in order to show the initial thermalization period. The lower figures show histograms and fitted Gaussian distributions for the values of the instantaneous pressure (lower left), temperature (middle figure) and box size ratio (lower right).

V. SUMMARY

The elasticity tensor of copper, modeled with a realistic tabulated EAM potential, was calculated using a single molecular dynamics simulation in the NVT ensemble, employing the stress-stress fluctuation formulation. It was shown that such calculations are accurate and robust and converge within a few thousand MD steps, with a relatively small number of particles (a few hundreds). The calculations were performed in the temperature range of 0-1000K and compared to experimental values, showing a good quantitative and qualitative agreement. The various thermal contributions to the values of the elastic constants were studied as a function of temperature.

The results suggest that this method can be applied to calculate local elastic constants of real crystalline materials for local regions embedded within large crystalline structure. In addition, it can improve the calibration process of inter-atomic potentials, which typically employ the explicit deformation method [8, 10, 16], that requires the generation of a consistent set of simulations under varying deformations, in order to obtain the elasticity tensor. The use of a single simulation, other than being simpler, convenient and accurate, has a lower risk for the spontaneous appearance of defects and other phases during direct force calculations.
Figure 4. (Color online) Components of the instantaneous Born stress tensor (upper figure, eq. 25) for an NVT simulation of Copper at $T = 300$K for which the volume is chosen such that the total pressure is zero (as obtained from Fig. 1). The lower figure shows the resulting histograms and fitted Gaussian distributions of the various Born stress tensor components.

[1] Murray S Daw and Michael I Baskes. Embedded-atom method: Derivation and application to impurities, surfaces, and other defects in metals. *Physical Review B*, 29(12):6443, 1984.
[2] Ralph J Wolf, Khalid A Mansour, Myung W Lee, and John R Ray. Temperature dependence of elastic constants of embedded-atom models of palladium. *Physical Review B*, 46(13):8027, 1992.
[3] T Çağın, G Dereli, M Uludoğan, and MEHMET Tomak. Thermal and mechanical properties of some fcc transition metals. *Physical review B*, 59(5):3468, 1999.
[4] Somchart Chantasiriwan and Frederick Milstein. Higher-order elasticity of cubic metals in the embedded-atom method. *Physical Review B*, 53(21):14080, 1996.
[5] John R Ray, Michael C Moody, and Aneesur Rahman. Molecular dynamics calculation of elastic constants for a crystalline system in equilibrium. *Physical Review B*, 32(2):733, 1985.
[6] DR Squire, AC Holt, and WG Hoover. Isothermal elastic constants for argon. theory and monte carlo calculations.
[7] JF Lutsko. Generalized expressions for the calculation of elastic constants by computer simulation. *Journal of applied physics*, 65(8):2991–2997, 1989.
[8] Germain Clavier, Nicolas Desbiens, Emeric Bourasseau, Véronique Lachet, Nadège Brusselle-Dupend, and Bernard Rousseau. Computation of elastic constants of solids using molecular simulation: comparison of constant volume and constant pressure ensemble methods. *Molecular Simulation*, 43(17):1413–1422, 2017.
[9] Dominik Lips and Philipp Maass. Stress-stress fluctuation formula for elastic constants in the npt ensemble. *Physical Review E*, 97(5):053002, 2018.
[10] Seyed Moein Rassoulinejad-Mousavi, Yijin Mao, and Yuwen Zhang. Evaluation of copper, aluminum, and nickel interatomic potentials on predicting the elastic properties. *Journal of Applied Physics*, 119(24):244304, 2016.
[11] Michael Griebel and Jan Hamaekers. Molecular dynamics simulations of the elastic moduli of polymer–carbon
Figure 5. (Color online) Upper figures - the Born elastic constants (eq. [26]): $C_{11}^B$ (left upper figure), $C_{12}^B$ (middle upper figure) and $C_{44}^B$ (right upper figure), for an NVT simulation of Copper at $T = 300K$ (as described in Fig. 4). The instantaneous value, cumulative average, convergence error and ratio of the standard deviation to the mean are shown, as is detailed in Fig. 2. The lower figures shows the resulting histograms and fitted Gaussian distributions.
Figure 6. Relative error between the instantaneous conserved energy and the initial value, for NPT (upper figure, eq. B8) and NVT (upper figure, eq. C15) molecular dynamics simulations of Copper at \( T = 300 \) K and zero pressure (the simulations described in figures 2-3 and 4-5, respectively).
Figure 7. (Color online) The different terms contributing to the total isothermal elastic constants $C_{11}$ (left pane), $C_{12}$ (middle pane) and $C_{44}$ (right pane) of Copper as a function of temperature (solid blue line) - the Born term (first term in eq. 21, dashed orange line), Born stress fluctuation term (minus the second term in eq. 21, dashed dotted green line) and the ideal gas kinetic term (minus the last term in eq. 21 dotted red line).

Figure 8. (Color online) The isothermal elastic constants $C_{11}$ (black), $C_{12}$ (red) and $C_{44}$ (blue) of Copper as a function of temperature. Solid lines represent molecular dynamics calculated values in the range 300-800K given in Ref. [43] for $C_{11}$ and $C_{12}$, and blue X data point represents a calculated value in the temperature range 300-800K given in Ref. [10]. The blue X data point represents experimental values in the temperature range 300-800K given in Ref. [10].

Appendix A: Elastic constants in the canonical ensemble

In the canonical ensemble, the free energy is given by:

$$\mathcal{F} = -k_B T \ln Z,$$

(A1)

where the canonical partition function is given by:

$$Z = \frac{1}{h^{3N}} \int d^3p^N \int d^3r^N e^{-\beta H(r^N,p^N)}$$

$$= \frac{1}{\prod_i \Lambda_i^3} \int d^3r^N e^{-\beta V(r^N)},$$

(A2)

where $\beta = 1/k_B T$ and $\Lambda_i = \left(\frac{2\pi \hbar^2}{m_i}\right)^{\frac{1}{2}}$ is the thermal de-Broglie wavelength. We note that in order to calculate strain derivatives (i.e. as in equations 12, 13), the $\prod_i \Lambda_i^3$ factor can be dropped, so that for the derivations presented in this appendix, we re-denote:

$$Z = \int d^3r^N e^{-\beta V(r^N)}.\quad (A3)$$

Consider the canonical average of a configurational operator $A = A(r^N)$:

$$\langle A \rangle = \frac{1}{Z} \int d^3r^N A(r^N) e^{-\beta V(r^N)}.$$  

(A4)

In order to evaluate the strain derivative $\frac{\partial \langle A \rangle}{\partial \eta_{\alpha \beta}}$, we write the integral in terms of the reference configuration coordinates $R$, since the strain derivative cannot be brought inside the integral, because the deformed volume $V$ depends on $\eta$. Therefore, we write:

$$\int_V d^3r^N A(r^N) e^{-\beta V(r^N)} = \int_{V_0} d^3R^N (\det J)^N A e^{-\beta V},$$

(A5)

where the integrand in the RHS is understood to be evaluated at $r(R)$. We can now write the strain derivative:

$$\frac{\partial}{\partial \eta_{\alpha \beta}} \int_V d^3r^N A(r^N) e^{-\beta V(r^N)} =$$

$$\int_{V_0} d^3R^N \frac{\partial}{\partial \eta_{\alpha \beta}} [(\det J)^N A e^{-\beta V}],$$

(A6)

the integrand reads:

$$\frac{\partial}{\partial \eta_{\alpha \beta}} [(\det J)^N A e^{-\beta V}] =$$

$$e^{-\beta V} (\det J)^N \left[ \frac{A}{\det J} \frac{\partial \det J}{\partial \eta_{\alpha \beta}} + \frac{\partial A}{\partial \eta_{\alpha \beta}} - \beta A \frac{\partial V}{\partial \eta_{\alpha \beta}} \right].$$
Using the well known rule for the derivative of a determinant:
\[ \frac{\partial \det (M)}{\partial M_{\alpha \beta}} = \det (M) M^{-T}_{\alpha \beta}, \quad (A7) \]
and eq. [3] it is readily shown that:
\[ \frac{1}{\det (J)} \frac{\partial \det (J)}{\partial \eta_{\alpha \beta}} = \frac{1}{\det (J)} D_{\alpha \beta} \det (J) = (2 \eta + I)^{-T}_{\alpha \beta}. \quad (A8) \]

As a result, eq. [A6] reads:
\[ \frac{\partial}{\partial \eta_{\alpha \beta}} \left( \int_V d^3r N \langle r^N \rangle e^{-\beta V(r^N)} \right) = \int_V d^3r N \langle \left( A(2 \eta + I)^{-T}_{\alpha \beta} + \frac{\partial A}{\partial \eta_{\alpha \beta}} - \beta A \frac{\partial V}{\partial \eta_{\alpha \beta}} \right) e^{-\beta V} \rangle. \quad (A9) \]

Using this for the particular case \( A = 1 \), one finds:
\[ \frac{1}{Z} \frac{\partial Z}{\partial \eta_{\alpha \beta}} = (2 \eta + I)^{-1}_{\alpha \beta} - \beta \left( \frac{\partial V}{\partial \eta_{\alpha \beta}} \right). \quad (A10) \]

Differentiation of eq. [A3] using the derivative product rule and equations [A9][A10] results in the general strain derivative rule:
\[ \frac{\partial \langle A \rangle}{\partial \eta_{\alpha \beta}} = \left\langle \frac{\partial A}{\partial \eta_{\alpha \beta}} \right\rangle - \beta \left[ \left\langle A \frac{\partial V}{\partial \eta_{\alpha \beta}} \right\rangle - \langle A \rangle \left\langle \frac{\partial V}{\partial \eta_{\alpha \beta}} \right \rangle \right]. \quad (A11) \]

For an EAM potential of the form [15] we can write:
\[ \frac{\partial V}{\partial \eta_{\alpha \beta}} = \sum_i \frac{\partial V}{\partial r_i} \cdot \frac{\partial r_i}{\partial \eta_{\alpha \beta}} = - \sum_i \frac{\partial V}{\partial r_i} \cdot \frac{\partial r_i}{\partial \eta_{\alpha \beta}} \]
\[ = - \sum_i \sum_{j \neq i} F_{ij} r_{ij, \gamma} \frac{\partial r_{ij, \gamma}}{\partial \eta_{\alpha \beta}} + \sum_i F_{ij} r_{ij, \gamma} \frac{\partial r_{ij, \gamma}}{\partial \eta_{\alpha \beta}} \]
\[ = - \frac{1}{2} \sum_i \sum_{j \neq i} F_{ij} r_{ij, \gamma} \frac{\partial r_{ij, \gamma}}{\partial \eta_{\alpha \beta}} - \frac{1}{2} \sum_i \sum_{j \neq i} F_{ij} \frac{\partial r_{ij}}{\partial \eta_{\alpha \beta}} \]
\[ = - \frac{1}{2} \sum_i \sum_{j \neq i} F_{ij} r_{ij, \gamma} \frac{\partial r_{ij, \gamma}}{\partial \eta_{\alpha \beta}} - \frac{1}{2} \sum_i \sum_{j \neq i} F_{ij} \frac{\partial r_{ij}}{\partial \eta_{\alpha \beta}} \]
where in the last term, the summation is over ordered pairs. From eq. [3] it is evident that:
\[ \frac{\partial r_{ij}}{\partial \eta_{\alpha \beta}} = 2R_\alpha R_\beta, \quad (A12) \]
and, more generally, for any radial function \( f = f(r) \), we have:
\[ D_{\alpha \beta} f = \frac{\partial f}{\partial \eta_{\alpha \beta}} = \frac{\partial f}{\partial \eta_{\beta \alpha}} = \frac{df}{dr} \frac{R_\alpha R_\beta}{r}. \quad (A13) \]

Hence, we can finally write:
\[ \frac{\partial V}{\partial \eta_{\alpha \beta}} = \frac{\partial V}{\partial \eta_{\beta \alpha}} = D_{\alpha \beta} V = - \sum_{i<j} F_{ij} \frac{R_{ij, \alpha} R_{ij, \beta}}{r_{ij}}. \quad (A14) \]

From eq. [A10] it follows that:
\[ \frac{\partial F}{\partial \eta_{\alpha \beta}} = \left( \frac{\partial V}{\partial \eta_{\beta \delta}} \right) - k_B T N \langle 2 \eta + I \rangle^{-T}_{\alpha \beta}, \quad (A15) \]
which is a symmetric tensor. Hence, eq. [A15] when evaluated at zero strain, proves equations 23 and 25.

Next, in order to evaluate the isothermal elastic constant defined by eq. [13] consider the second derivative tensor:
\[ D_{\alpha \beta} D_{\gamma \delta} F = D_{\alpha \beta} \left[ \langle \frac{\partial V}{\partial \eta_{\gamma \delta}} \rangle - k_B T N \langle 2 \eta + I \rangle^{-T}_{\gamma \delta} \right]. \quad (A16) \]

In order to evaluate the second term, we use the following identity for the derivative of a matrix inverse:
\[ \frac{\partial M_{\gamma \delta}^{-1}}{\partial \eta_{\alpha \beta}} = -M_{\delta \alpha}^{-1} M_{\beta \gamma}^{-1}, \quad (A17) \]
which results in the relation:
\[ \frac{\partial}{\partial \eta_{\alpha \beta}} \left( \frac{\partial^2 V}{\partial \eta_{\gamma \delta}} \right) = \left[ \frac{\partial^2 V}{\partial \eta_{\gamma \delta}} \right] - \beta \left[ \left( \frac{\partial^2 V}{\partial \eta_{\gamma \delta}} \right) - \langle \frac{\partial^2 V}{\partial \eta_{\gamma \delta}} \rangle \right]. \quad (A19) \]

We note that the second term is a symmetric tensor with respect to \( \alpha \leftrightarrow \beta \) and \( \gamma \leftrightarrow \delta \). In order to evaluate the first term, we differentiate eq. [A14]
\[ \frac{\partial^2 V}{\partial \eta_{\alpha \beta} \partial \eta_{\gamma \delta}} = \frac{\partial}{\partial \eta_{\alpha \beta}} \left( - \sum_{i<j} F_{ij} R_{ij, \gamma} R_{ij, \delta} \right) \]
\[ = - \sum_{i<j} \left[ R_{ij, \gamma} R_{ij, \delta} \frac{\partial F_{ij}}{\partial \eta_{\alpha \beta}} + R_{ij, \gamma} R_{ij, \delta} F_{ij} \frac{\partial}{\partial \eta_{\alpha \beta}} \left( \frac{1}{r_{ij}} \right) \right]. \quad (A20) \]

Using the identity [A13] we get:
The equations of motion for the

\[
\frac{\partial}{\partial \eta_{\alpha \beta}} \left( \frac{1}{r} \right) = - \frac{R_{\alpha} R_{\beta}}{r^3},
\]

(A21)

and using eq. [17] and the identity [A13] gives:

\[
\frac{\partial F_{ij}}{\partial \eta_{\alpha \beta}} = (r''(r_{ij}) + [F'(\rho_i) + F'(\rho_j)] \rho''(r_{ij}) \left. \frac{R_{ij,\alpha} R_{ij,\beta}}{r_{ij}} \right) + \rho'(r_{ij}) \frac{\partial}{\partial \eta_{\alpha \beta}} [F'(\rho_i) + F'(\rho_j)].
\]

(A22)

In order to evaluate the last term in eq. [A22] we write:

\[
\frac{\partial F'(\rho_i)}{\partial \eta_{\alpha \beta}} = F''(\rho_i) \frac{\partial \rho_i}{\partial \eta_{\alpha \beta}} = F''(\rho_i) \sum_{k \neq i} \frac{\partial \rho}{\partial \eta_{\alpha \beta}} \left( R_{ik,\alpha} R_{ik,\beta} \right) r_{ik}^{-2},
\]

(A23)

where in the last step the identity [A13] was used again. Plugging equations [A21] [A22] back into eq. [A20] gives:

\[
\frac{\partial^2 \mathcal{V}}{\partial \eta_{\alpha \beta} \partial \eta_{\gamma \delta}} = D_{\alpha \beta} D_{\gamma \delta} \mathcal{V} + \sum_{i<j} X_{ij} R_{ij,\alpha} R_{ij,\beta} R_{ij,\gamma} R_{ij,\delta} r_{ij}^{-2} + \sum_i \left( \sum_{k \neq i} \left( R_{ik,\alpha} R_{ik,\beta} \rho'(r_{ik}) \right) \left( \sum_{k \neq i} \left( R_{ik,\alpha} R_{ik,\beta} \rho'(r_{ik}) \right) \right) \right),
\]

(A24)

where \( X_{ij} \) is defined by eq. [27] and we have used the fact that the resulting expression defines a symmetric tensor with respect to \( \alpha \leftrightarrow \beta \) and \( \gamma \leftrightarrow \delta \).

Finally, when evaluated at zero strain (\( \eta = 0, R = r \)), the combination of equations [A10] [A18] [A19] and [A21] proves the relations [26] [28].

Appendix B: Equations of motion in the NVT ensemble

In this appendix we list the equations of motion of the widely used Nose-Hoover-Chains method in the isothermal-isobaric (NVT) ensemble [22] [25] [27], which was used in the calculations performed in this work. We use a chain of \( M \) thermostats with coordinates \( \eta_j \) and momenta \( p_{\eta_j} \). The equations of motions for the \( i = 1...N \) particles are:

\[
\frac{dp_i}{dt} = F_i - \left( \frac{p_{\eta_i}}{Q_i} \right) p_i,
\]

(B1)

\[
\frac{dr_i}{dt} = \frac{p_i}{m_i},
\]

(B2)

The equations of motion for the \( j = 1...M \) thermostat variables are given by:

\[
\frac{d\eta_j}{dt} = \frac{p_{\eta_j}}{Q_j},
\]

(B3)

\[
\frac{dp_{\eta_j}}{dt} = \left( G_j - \frac{p_{\eta_{j+1}}}{Q_{j+1}} \right) p_{\eta_j}, \quad j = 1...M - 1
\]

\[
\frac{dp_{\eta_M}}{dt} = \left( G_M - \frac{p_{\eta_1}}{Q_1} \right) p_{\eta_M},
\]

(B4)

where the forces are:

\[
G_j = \left\{ \begin{array}{ll}
\sum_{i=1}^N \frac{p_i^2}{2M} - gk_BT, & j = 1 \\
\sum_{i=1}^N \frac{p_i^2}{2M} - k_BT, & j = 2...M
\end{array} \right.
\]

(B5)

with the number of degrees of freedom:

\[
g = 3(N-1).
\]

(B6)

The thermostat “masses” \( Q_j \) can be written in terms of a thermostat relaxation timescale \( \tau_T \) [28]:

\[
Q_j = \left\{ \begin{array}{ll}
gk_BT \tau_T^2, & j = 1 \\
k_BT \tau_T^2, & j = 2...M
\end{array} \right.
\]

(B7)

The non-Hamiltonian system B1-B4 has the conserved quantity [26] [28]:

\[
E_{\text{cons}} = \mathcal{H} + \sum_{j=1}^M \frac{p_{\eta_j}^2}{2Q_j} + gk_BT\eta_1 + \sum_{j=2}^M k_BT\eta_j,
\]

(B8)

where \( \mathcal{H} \) is the true Hamiltonian given by eq. [14].

Appendix C: Equations of motion in the NPT ensemble

In this appendix we list the equations of motion in the widely used Nose-Hoover-Chains method in the isothermal-isobaric (NPT) ensemble [22] [25] [27], which was used in the calculations performed in this work. As in appendix [B], we use a chain of \( M \) thermostats whose coordinates and momenta are \( \eta_j \) and \( p_{\eta_j} \), which are coupled to the equations of motion of the \( N \) particles. In the NPT ensemble, the volume \( V = V(t) \) is treated as a dynamical variable via the generalized coordinate:

\[
\epsilon(t) = \frac{1}{3} \ln \left( \frac{V(t)}{V(0)} \right),
\]

(C1)

whose momentum \( p_\epsilon \) is coupled to an additional chain of \( M' \) thermostats with coordinates \( \eta'_j \) and momenta \( p'_{\eta_j} \). The equations of motions for the \( i = 1...N \) particles are:

\[
\frac{dr_i}{dt} = \frac{p_i}{m_i} + \frac{p_\epsilon}{W} r_i,
\]

(C2)

\[
\frac{dp_i}{dt} = F_i - \left( 1 + \frac{3}{g} \right) \left( \frac{p_i}{W} \right) p_i - \left( \frac{p_{\eta_i}}{Q_i} \right) p_i,
\]

(C3)

The equations of motion for the barostat variables are:
\[
\frac{dc}{dt} = \frac{p_c}{W}, \quad \text{(C4)}
\]

\[
\frac{dp_c}{dt} = 3 \left( P_{\text{inst}} V - PV \right) + 3 \sum_{i=1}^{N} \frac{p_i^2}{2m_i} - \left( \frac{p_{\eta_j}}{Q_1} \right) p_c, \quad \text{(C5)}
\]

where \( P \) is the applied external pressure and the instantaneous pressure is given by the virial theorem:

\[
P_{\text{inst}} V = \frac{1}{3} \sum_i p_i^2 m_i + \frac{1}{3} \sum_{i<j} F_{ij} r_{ij}. \quad \text{(C6)}
\]

The equations of motion for the \( j = 1 \ldots M \) particle-coupled thermostat variables are given by:

\[
\frac{d\eta_j}{dt} = \frac{p_{\eta_j}}{Q_j}, \quad \text{(C7)}
\]

\[
\frac{dp_{\eta_j}}{dt} = \begin{cases} G_j - \left( \frac{p_{\eta_{j+1}}}{Q_{j+1}} \right) p_{\eta_j}, & j = 1 \ldots M - 1 \\ G_M, & j = M \end{cases} \quad \text{(C8)}
\]

where the forces are:

\[
G_j = \begin{cases} \sum_i \frac{p_i^2}{m_i} - k_B T, & j = 1 \\ \frac{p_{\eta_{j-1}}^2}{Q_{j-1}} - k_B T, & j = 2 \ldots M \end{cases} \quad \text{(C9)}
\]

The equations of motion for the \( j = 1 \ldots M' \) barostat-coupled thermostat variables are given by:

\[
\frac{dp_{\eta'_j}}{dt} = \begin{cases} G'_j - \left( \frac{p_{\eta'_{j+1}}}{Q'_{j+1}} \right) p_{\eta'_j}, & j = 1 \ldots M' - 1 \\ G'_{M'}, & j = M' \end{cases} \quad \text{(C10)}
\]

where the forces are:

\[
G'_j = \begin{cases} \frac{p^2}{W} - k_B T, & j = 1 \\ \frac{p_{\eta'_{j-1}}^2}{Q'_{j-1}} - k_B T, & j = 2 \ldots M' \end{cases} \quad \text{(C11)}
\]

The particle-coupled thermostat masses \( Q_j \) are given in terms of a thermostat relaxation timescale \( \tau_T \) as in B7, while the barostat mass \( W \) and the barostat-coupled thermostat masses \( Q'_j \) are written in terms of a barostat relaxation timescale \( \tau_p \) as 23 28:

\[
W = g k_B T \tau_p^2, \quad \text{(C13)}
\]

\[
Q'_j = k_B T \tau_{p_j}^2. \quad \text{(C14)}
\]

The non-Hamiltonian system C2-C11 has the conserved quantity 22 25 26:

\[
E_{\text{cons}} = \mathcal{H} + PV + \frac{p_c^2}{2W} + \sum_{j=1}^{M} \frac{p_{\eta_j}^2}{2Q_j} + \sum_{j=1}^{M'} \frac{p_{\eta'_j}^2}{2Q'_j}
\]

\[
+ g k_B T \eta_1 + \sum_{j=2}^{M} k_B T \eta_j + \sum_{j=1}^{M'} k_B T \eta'_j. \quad \text{(C15)}
\]