ETH Zurich
Department of Mechanical and Process Engineering
Statistical Mechanics of Elasticity
Exercises 8 and 9 - Summer 2007

Institute for Mechanical Systems
Center of Mechanics
Prof. Dr. Sanjay Govindjee
Felix Hildebrand

Useful Definitions

Equilibrium lattice configurations

At *zero* absolute temperature T, the equilibrium configuration of a periodic atomic structure parametrized by ξ_i is obtained from a minimization of the potential energy $U(\xi_i)$ with respect to ξ_i. At *non-zero* absolute temperature T, the equilibrium configuration of a periodic atomic structure is obtained from a minimization of the free energy $\Psi(\mathbf{F}, T)$, where $\mathbf{F}$ is the deformation gradient.

Quasiharmonic approximation

The thermal vibrations of atoms in a lattice can be approximated by thermal vibrations about the lattice sites (stretched by the macroscopic deformation gradient $\mathbf{F}$ according to Cauchy-Born) if the temperature T of the system is sufficiently low. The partition function can then be approximated by

$$Z_{qh}(\mathbf{F}, T) = (2\pi kT)^n \exp\left(-\frac{U_o(\mathbf{F})}{kT}\right) \prod_{r=1}^{n} \frac{1}{\omega_r(\mathbf{F})}, \tag{1}$$

where ω_r^2 are the n generalized eigenvalues of

$$\omega^2 \mathbf{M}\mathbf{a} = \mathbf{K}\mathbf{a} \qquad \text{with} \qquad K_{ij} = \left.\frac{\partial^2 U(\mathbf{F}, q_k)}{\partial q_i \partial q_j}\right|_{q_k=0} \tag{2}$$

where $\mathbf{M}$ and $\mathbf{K}$ are the $n \times n$ mass and stiffness matrices of the n-degree of freedom system, respectively and where the q_j describe the deviation of the atomic positions from the lattice sites (stretched by $\mathbf{F}$). The quasiharmonic approximation of the free energy thus takes the form

$$\Psi_{qh}(\mathbf{F}, T) = -kT \log(Z_{qh}(\mathbf{F}, T)) = U_o(\mathbf{F}) - nkT \log(2\pi kT) + kT \sum_{r=1}^{n} \log(\omega_r(\mathbf{F})), \tag{3}$$

and the resulting stress-strain relation is (V_o is the reference volume of the system)

$$\mathbf{P}_{qh}(\mathbf{F}, T) = \frac{1}{V_o} \frac{\partial \Psi_{qh}(\mathbf{F}, T)}{\partial \mathbf{F}} = \frac{1}{V_o} \left[\frac{\partial U_o(\mathbf{F})}{\partial \mathbf{F}} + kT \sum_{r=1}^{n} \frac{\partial \omega_r(\mathbf{F})}{\partial \mathbf{F}}\right]. \tag{4}$$

The Morse potential

Qualitatively somewhat similar to the Lennard-Jones potential, the Morse potential has the form

$$\phi(r) = u_o \left[e^{-2a_o(r/r_o - 1)} - 2e^{-a_o(r/r_o - 1)}\right], \tag{5}$$

where u_o is the energy at distance r_o and a_o is a measure for the linear stiffness around r_o (see Figure 1).

Useful trigonometric identities

The following trigonometric identities might be useful for the homework problem

$$\sin(\alpha + \beta) = \sin(\alpha)\cos(\beta) + \sin(\beta)\cos(\alpha), \qquad \sin(\alpha - \beta) = \sin(\alpha)\cos(\beta) - \sin(\beta)\cos(\alpha),$$
$$1 - \cos(\alpha) = 2\sin^2\left(\frac{\alpha}{2}\right),$$

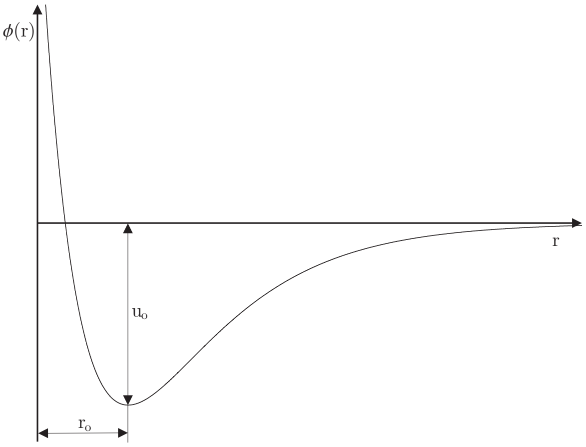

Figure 1: The Morse potential.

Problem 1 - Linear chain with fixed boundary conditions

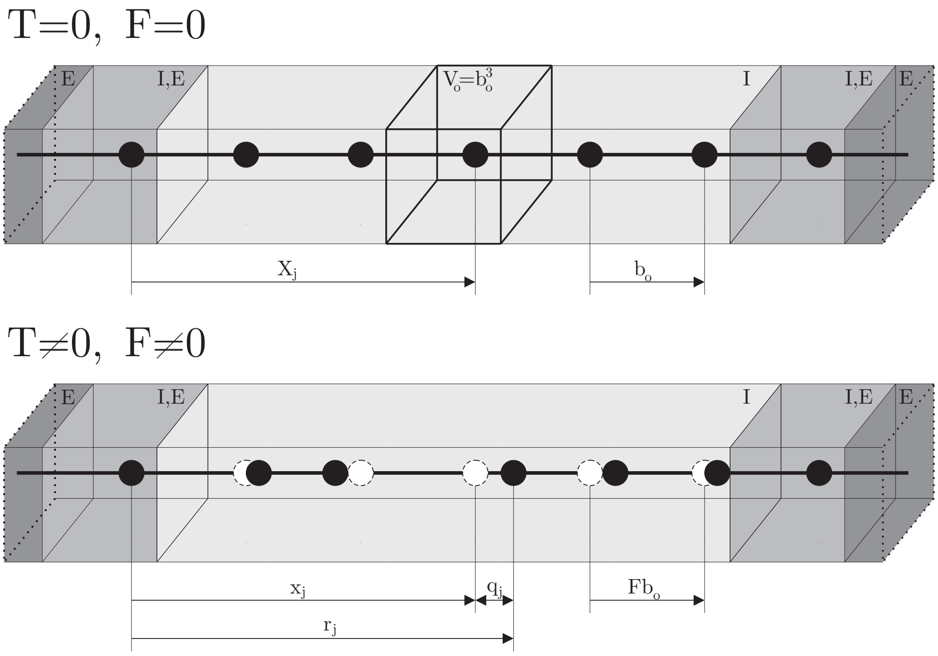

Figure 2: Reference and current configuration of a chain with fixed boundary conditions.

Consider a one-dimensional linear chain of like atoms. Pick a representative "interior region" I consisting of N atoms and adjacent regions I, E that contain the atoms interacting with the chain (see Figure 2). Let the positions in the reference configuration (stress free, $T = 0K$) be denoted by

$$X_j = jb_o, \tag{6}$$

where b_o is the lattice parameter and j the number of the atom. For dimensional reasons, each atom is associated with a reference volume of $V_o = b_o^3$. Let the position in the current configuration (deformed, $T \neq 0$) be denoted by

$$r_j = x_j + q_j = FX_j + q_j = Fb_o j + q_j, \tag{7}$$

where x_j are the lattice sites stretched by the one-dimensional deformation gradient F (according to Cauchy-Born) and where the q_j denote the deviation caused by thermal vibration. Atoms have masses m and their interaction is described by pair potentials $\phi(r)$, where r is the respective interatomic distance. Throughout the calculations, assume that the atoms interact only with their nearest neighbors and that atoms in I, E do not thermally vibrate.

The goal of this exercise is to derive the quasiharmonic approximation of the free energy, $\Psi_{qh}(F, T)$, and to calculate an approximation of the thermal expansion and the thermoelastic stress-strain relation from it. To do so, carry out the following steps:

a) Derive the potential energy $U(b_o)$ of the reference lattice and determine b_o from $\phi(r)$.

b) Derive an expression for the potential energy $U(F; q_j)$ in the current configuration. Carry out a Taylor expansion up to second order about $q_j = 0$ and compute all terms in terms of $\phi(r)$.

c) Derive the equations of motion of the atoms, i.e. $q_j(t)$, by assuming harmonic vibrations about $q_j = 0$.

d) Insert the ansatz

$$q_j(t) = a_j \cos(\omega t) \text{ and } a_j = B\cos(kx_j) + C\sin(kx_j), \tag{8}$$

where ω is the angular frequency and k the wave number. Use the boundary conditions to extract information on B and C and derive the dispersion relation

$$\omega^2 = \frac{2\phi''(Fb_o)}{m}(1 - \cos kFb_o) = \frac{4\phi''(Fb_o)}{m}\sin^2\left(\frac{kFb_o}{2}\right) \tag{9}$$

using the given trigonometric identities.

e) Use the fixed boundary conditions, the orthogonality condition

$$a_{rj}a_{sj} = \delta_{rs} \tag{10}$$

(where j is the atom number and r, s denote modes of vibration) and the dispersion relation to find the N wavenumbers k_r, the N eigenfrequencies ω_r and the corresponding N eigenvectors a_{rj} (including constants B_r and C_r) again using the given trigonometric identities.

f) Decouple the motions of the atoms by transforming to the normal modes and derive the partition function of the linear chain $Z(F, T)$.

g) Compute the free energy

$$\Psi(F, T) = -kT \log\left(Z(F, T)\right). \tag{11}$$

h) Explain how to compute the thermal expansion of the lattice, $F(T)$.

i) Derive an expression for the stress using

$$P = \frac{1}{V_o}\frac{\partial\Psi(F, T)}{\partial F}. \tag{12}$$

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Homework 1 - Linear chain with periodic boundary conditions

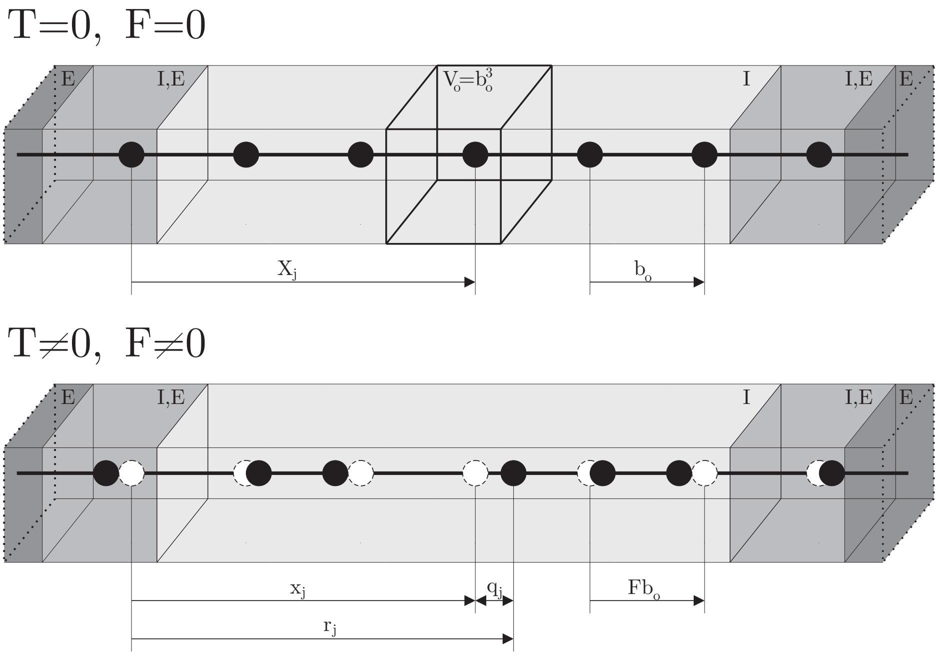

Figure 3: Reference and current configuration of a chain with periodic boundary conditions.

Again consider a one-dimensional linear chain of like atoms. Pick a representative "interior region" I consisting of $N = 101$ atoms and adjacent regions I, E that contain the atoms interacting with the chain (see Figure 3). Let the positions in the reference configuration (stress free, $T = 0K$) be denoted by

$$X_j = jb_o, \tag{13}$$

where b_o is the reference lattice parameter and j the number of the atom. For dimensional reasons, each atom is associated with a reference volume of $V_o = b_o^3$. Let the position in the current configuration (deformed, $T \neq 0$) be denoted by

$$r_j = x_j + q_j = FX_j + q_j = Fb_oj + q_j, \tag{14}$$

where x_j are the lattice sites stretched by the one-dimensional deformation gradient F (according to Cauchy-Born) and where the q_j denote the deviation caused by thermal vibration. The atoms have masses $m = 10^{-26}kg$ and their interaction is described by the so-called Morse potential

$$\phi(r) = u_o \left[e^{-2a_o(r/r_o-1)} - 2e^{-a_o(r/r_o-1)} \right], \tag{15}$$

where $u_o = 9 \cdot 10^{-17}J$, $a_o = 0.05$ and $r_o = 10^{-9}m$ are material parameters and r is the respective interatomic distance. Throughout the calculations, assume that the atoms interact only with their nearest neighbors and that atoms in I, E move according to periodic boundary conditions, i.e. $q_0 = q_N$ and $q_{N+1} = q_1$.

The goal of this exercise is to derive the quasiharmonic approximation of the free energy, $\Psi_{qh}(F, T)$, and to calculate an approximation of the thermal expansion and the thermoelastic stress-strain relation from it. To do so, carry out the following steps:

a) Derive the potential energy $U(b_o)$ of the reference lattice and determine the numerical value of b_o by minimizing it.

b) Derive an expression for the potential energy $U(F; q_j)$ in the current configuration (remember to add only half the energy between I and I, E as the other half belongs to “the next chain”). Carry out a Taylor expansion up to second order about $q_j = 0$ and compute all terms of the stiffness matrix K_{ij} using $\phi(r)$ (and not substituting the Morse potential). Make sure you get the right components K_{1N} and K_{N1}.

c) State the equations of motion of the atoms by assuming harmonic vibrations about $q_j = 0$.

d) Now solve the generalized eigenvalue problem derived in c) numerically (for $F = 1$). Look at the first 5 eigenvalues and plot the corresponding eigenmodes. What do you observe? What does the eigenmode corresponding to the lowest eigenvalue stand for physically? Why didn’t this come up in the case of the fixed boundary conditions? Should this also be summed over when calculating the partition function and the free energy?

e) By looking at the eigenmodes, one can easily see they have the following structure:

$$a_{ij} = \begin{cases} B_i \cos\left(\frac{\pi(i-1)(j)}{N}\right) & \text{for i odd} \\ B_i \sin\left(\frac{\pi(i)(j)}{N}\right) & \text{for i even} \end{cases} \qquad i, j = \{1, ..., N\}, \tag{16}$$

where the B_i are chosen such that the a_{ij} are normalized. Of course the pairs of $\sin$ and $\cos$ functions corresponding to equal eigenvalues ω can be flipped. What are thus the $(N-1)/2$ wavevectors k_r corresponding to the $(N-1)/2$ pairs of eigenvalues ω_r? Plot the dispersion relation for the reference configuration, i.e. $F = 1$.

f) Compute the free energy for a given F (keep in mind that the eigenvalue problem has to be solved anew for each choice of F)

$$\Psi(F, T) = U_o(\mathbf{F}) - nkT \log(2\pi kT) + kT \sum_{r=1}^{n} \log(\omega_r(\mathbf{F})) \tag{17}$$

and remember to only sum over eigenvalues representing thermal *vibration*.

g) Compute the thermal expansion of the lattice, $F(T)$, for the given interaction potential by minimizing $\Psi(F, T)$ for given a T (using, e.g. *fminsearch*). Plot the resulting values for $0K \leq T \leq 1000K$ (with incements of $\Delta T = 10K$).

h) Calculate the stress-strain relation numerically using

$$P(F, T) = \frac{1}{V_o} \frac{\partial \Psi(F, T)}{\partial F} \approx \frac{1}{V_o} \frac{\Psi(F + \Delta F, T) - \Psi(F, T)}{\Delta F} \tag{18}$$

and use $\Delta F = 0.00001$. Make a mesh plot of $P(F, T)$ for $0K \leq T \leq 1000K$ and $0.99 \leq F \leq 1.01$ using increments of $\Delta T = 10K$ and $\Delta F = 0.0001$. In the same plot, plot the function $P_o(F, T) = 0$. What geometrically defines the thermal expansion in this plot?

Questions/Comments/Suggestions? Felix Hildebrand - CLA H23.1 - 044/632-7755 - felixhi@ethz.ch