

Statistical Mechanics

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Outline

- Motivation
- Statistical ensembles
- Definition of temperature

Ref: *Introduction to Modern
Statistical Mechanics*
by D. Chandler

Motivation

- What is nanotechnology?
 - ◆ Enabled by unique subcontinuum effects
- Why are statistical mechanics relevant?
 - ◆ Engineers seek useful macroscopic effects and behavior from nanoscopic features and phenomena
 - ◆ Studying the collective behavior of nanoscopic entities becomes essential

Statistical Ensembles

- Consider a collection of particles characterized by its number of particles N , volume V , and energy E
- The collection can exist in a variety (or ensemble) of states in which the foregoing variables may change
- Fundamental premise of statistical mechanics...
 - ◆ during a measurement (e.g, of temperature), every possible state does in fact occur such that observed properties are averages of all possible states

The Microcanonical Ensemble

- Density of states

$\Omega(N, V, E) \equiv$ number of possible states with particle number N , volume V , and energy between E and $E+dE$

- Statistical assumption

All states are equally probable

- Probability that a state $\nu = (N, V, E)$ exists

$$P_\nu = 1/\Omega(N, V, E)$$

- The collection of states with fixed N, V, E is called the microcanonical ensemble

Entropy

- A measure of system disorder
- 2nd Law of Thermodynamics states that disorder is maximized in real processes

- Statistical definition

$$S = k_B \ln(\Omega)$$

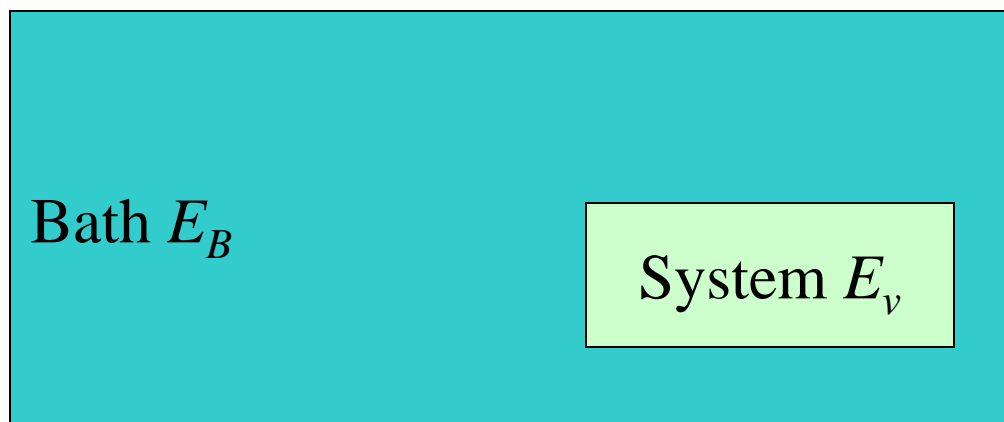
- Definition of temperature

$$1/T = (\partial S / \partial E)_{N,V} \quad \text{or}$$

$$\beta = (k_B T)^{-1} = (\partial \ln \Omega / \partial E)_{N,V}$$

Canonical Ensemble

- Collection of possible states with fixed N, V
 - ◆ Energy constraint is relaxed
- Consider a canonical system surrounded by a bath such that the system + bath is a microcanonical ensemble (fixed energy)



System + bath
With fixed
 N, V, E

Canonical Ensemble, cont'd

- 1st Law of Thermodynamics

$$E = E_B + E_v$$

- Consider the system in one definite state v
- The number of possible bath states is thus

$$\Omega(E_B) = \Omega(E - E_v)$$

- We expect the probability of system state v to be proportional to the corresponding number of bath states

$$P_v \sim \Omega(E - E_v) = \exp[\ln \Omega(E - E_v)]$$

- Taylor expansion for $E_v \ll E$:

$$\ln \Omega(E - E_v) \rightarrow \ln \Omega(E) - E_v (\partial \ln \Omega / \partial E)$$

- Result: $P_v \sim \exp(-\beta E_v)$

Normalization

- Sum of probabilities must equal 1

$$\sum P_v = 1$$

- Thus define the canonical partition function, Q

$$P_v = Q^{-1} \exp(-\beta E_v), \quad Q = \sum \exp(-\beta E_v)$$

- Averages

$$\begin{aligned} \langle E \rangle &= \langle E_v \rangle = \sum_v P_v E_v \\ &= \frac{\sum_v E_v e^{-\beta E_v}}{\sum_{v'} e^{-\beta E_{v'}}} \\ &= -\frac{\left(\frac{\partial Q}{\partial \beta} \right)_{N,V}}{Q} = -\left(\frac{\partial \ln Q}{\partial \beta} \right)_{N,V} \end{aligned}$$

Generalized Ensembles

- We know that the thermodynamic state of a system depends on two independent thermodynamic properties, e.g.,

$$k_B^{-1} dS = \beta dE + \xi dX$$

where, for example, X could represent N , the particle number (in which case, ξ is $-\beta\mu$)

- If we now allow E and X (e.g., N) to vary in the system, with a fixed value of Y (e.g., V), then we can show

$$P_\nu = \frac{\exp(-\beta E_\nu - \xi X_\nu)}{\Xi} \quad \langle E \rangle = - \left(\frac{\partial \ln \Xi}{\partial \beta} \right)_{\xi, Y}$$

$$\text{where } \Xi = \sum_\nu \exp(-\beta E_\nu - \xi X_\nu) \quad \langle X \rangle = - \left(\frac{\partial \ln \Xi}{\partial \xi} \right)_{\beta, Y}$$

Grand Canonical Ensemble

- Allows E and N to vary (fixed V)

Partition function: $\Xi = \sum \exp [-\beta(E_v - \mu N_v)]$

Where v denotes a state with N_v particles and energy E_v

- Occupation numbers

- ◆ A given state will have n_1 particles with energy ε_1 , n_2 particles with energy ε_2 , and so on...

- ◆ Bose-Einstein statistics allows integer occupation numbers
 $n_i = 0, 1, 2, 3, \dots$

- ◆ Fermi-Dirac statistics allows only binary occupation numbers
 $n_i = 0$ or 1

- Average occupation numbers

$\langle n_i \rangle = [\exp(\beta(\varepsilon_i - \mu)) - 1]^{-1}$ Bose-Einstein

$\langle n_i \rangle = [\exp(\beta(\varepsilon_i - \mu)) + 1]^{-1}$ Fermi-Dirac

Comments on Energy/Hamiltonian

- We will frequently refer to the Hamiltonian, defined as the sum of kinetic and potential energy
- In the classical context, the Hamiltonian of a harmonic oscillator can be expressed simply as

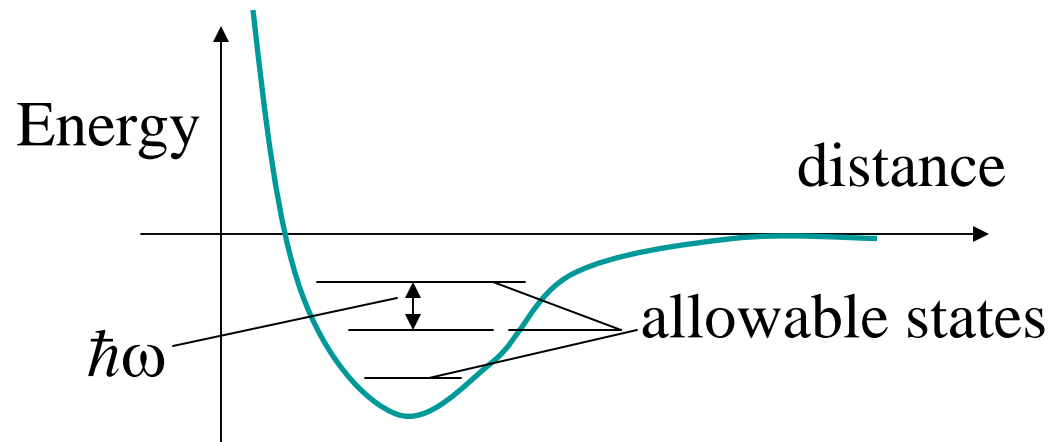
$$H_{classical} = \underbrace{\frac{p^2}{2m}}_{kinetic} + \underbrace{\frac{g}{2}u^2}_{potential} = E_{tot}$$

- In the quantum context, only a finite number of frequencies are allowed (i.e., the energies are quantized such that

$$H_{quantum} = \frac{p_{op}^2}{2m} + \frac{m\omega^2}{2}u_{op}^2 = \frac{1}{2m} \left(-i\hbar \frac{d}{dx} \right)^2 + \frac{m\omega^2}{2}u^2$$

such that $H_{quantum} \Psi = E\Psi$

Phonon Quantization



- For a simple (classical) harmonic oscillator, vibrational energy $\sim 0.5gu^2$ (continuous)
- However, for a quantum oscillator, only discrete energies are allowed, separated by $\hbar\omega$

The Virial Theorem

- The Virial Theorem is a result (a quite important one) of many-body physics
- It relates the average, total (i.e., summed) kinetic energy to the total potential of a many-body system

$$2\langle KE \rangle = \langle \mathbf{u} \cdot \nabla_{\mathbf{u}} U(\mathbf{u}) \rangle$$

where KE and U represent the total kinetic and potential energies

- Then, using the result from quantum mechanics:

$$\langle H \rangle = \langle KE \rangle + \langle U(\mathbf{u}) \rangle = \hbar\omega \left(n + \frac{1}{2} \right)$$

- We find that

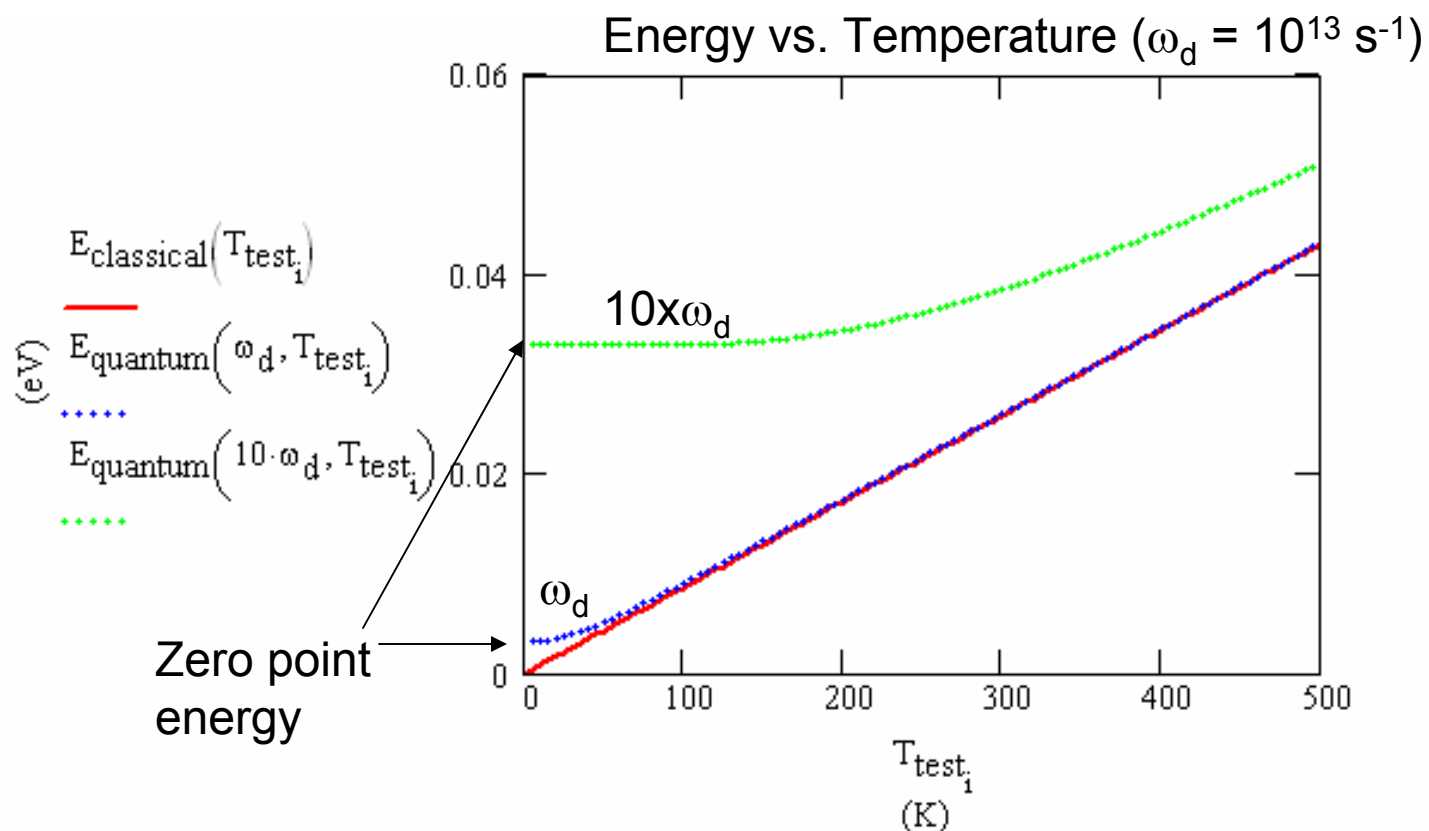
$$\langle KE \rangle = \langle U(\mathbf{u}) \rangle = \frac{1}{2} \hbar\omega \left(n + \frac{1}{2} \right)$$

- ♦ where n is the occupation number of phonons of a given wavevector and branch

Quantum and Classical Energies

Classical: $\langle E_{\text{tot}} \rangle = k_B T$ (independent of frequency, from equipartition principle)

Quantum: $\langle E_{\text{tot}} \rangle = \langle H \rangle = \hbar\omega [n(\omega, T) + \frac{1}{2}]$



So, What is Temperature?

- Clearly, temperature is intimately related to energy in both classical and quantum systems
- For a simple (classical) harmonic oscillator, the relationship is direct: $\langle E_{\text{tot}} \rangle = k_B T$
- For a quantum harmonic oscillator, the temperature dependence is buried in the occupation number: $\langle E_{\text{tot}} \rangle = \hbar\omega [n(\omega, T) + \frac{1}{2}]$
- Further, an atomic lattice can support *many* harmonic oscillators (see dispersion curve), and we need to sum over all of their frequencies to find temperature