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**
  \[ \Omega(N, V, E) \equiv \text{number of possible states with particle number } N, \text{ volume } V, \text{ and energy between } E \text{ and } E+dE \]

- **Statistical assumption**
  All states are equally probable

- **Probability that a state** \( \nu = (N, V, E) \) **exists**
  \[ P_{\nu} = \frac{1}{\Omega(N, V, E)} \]

- **The collection of states** with fixed \( N, V, E \) is called the microcanonical ensemble
Entropy

- A measure of system disorder
- 2\textsuperscript{nd} Law of Thermodynamics states that disorder is maximized in real processes
- Statistical definition
  \[ S = k_B \ln(\Omega) \]
- Definition of temperature
  \[ \frac{1}{T} = \left( \frac{\partial S}{\partial E} \right)_{N,V} \quad \text{or} \]
  \[ \beta = (k_B T)^{-1} = \left( \frac{\partial \ln \Omega}{\partial E} \right)_{N,V} \]
**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)

![Diagram of Canonical Ensemble](image)
Canonical Ensemble, cont’d

• 1\textsuperscript{st} Law of Thermodynamics
  \[ E = E_B + E_v \]
• Consider the system in one definite state \( \nu \)
• The number of possible bath states is thus
  \[ \Omega(E_B) = \Omega(E-E_v) \]
• We expect the probability of system state \( \nu \) to be proportional to the corresponding number of bath states
  \[ P_\nu \sim \Omega(E-E_v) = \exp[\ln \Omega(E-E_v)] \]
• Taylor expansion for \( E_v \ll E \):
  \[ \ln \Omega(E-E_v) \to \ln \Omega(E) - E_v \left( \partial \ln \Omega / \partial E \right) \]
• Result:
  \[ P_\nu \sim \exp(-\beta E_v) \]
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
  \[ \langle E \rangle = \langle E_v \rangle = \sum_v P_v E_v \]
  \[ = \sum_v E_v e^{-\beta E_v} \sum_{v'} e^{-\beta E_{v'}} \]
  \[ = -\left( \frac{\partial Q}{\partial \beta} \right)_{N,V} = -\left( \frac{\partial \ln Q}{\partial \beta} \right)_{N,V} \]
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, \( \xi \) 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

\[
P_v = \frac{\exp(-\beta E_v - \xi X_v)}{\Xi} \quad \langle E \rangle = -\left( \frac{\partial \ln \Xi}{\partial \beta} \right)_{\xi,Y} \\
\text{where} \quad \Xi = \sum_v \exp(-\beta E_v - \xi X_v) \quad \langle X \rangle = -\left( \frac{\partial \ln \Xi}{\partial \xi} \right)_{\beta,Y}
\]
Grand Canonical Ensemble

• Allows $E$ and $N$ to vary (fixed $V$)
  
  Partition function:  
  \[ \Xi = \sum \exp \left[ -\beta (E_v - \mu N_v) \right] \]
  
  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 $\varepsilon_1$, $n_2$ particles with energy $\varepsilon_2$, and so on…
  
  ♦ Bose-Einstein statistics allows integer occupation numbers
    
    \[ n_i = 0, 1, 2, 3, \ldots \]
  
  ♦ Fermi-Dirac statistics allows only binary occupation numbers
    
    \[ n_i = 0 \text{ or } 1 \]

• Average occupation numbers
  
  \[ <n_i> = [\exp(\beta(\varepsilon_i - \mu)) - 1]^{-1} \] Bose-Einstein
  
  \[ <n_i> = [\exp(\beta(\varepsilon_i - \mu) + 1]^{-1} \] 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

\[
H_{\text{classical}} = \frac{p^2}{2m} + \frac{g}{2}u^2 = E_{\text{tot}}
\]

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

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

such that \( H_{\text{quantum}} \Psi = E \Psi \)
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: $<E_{\text{tot}}> = k_B T$ (independent of frequency, from equipartition principle)
Quantum: $<E_{\text{tot}}> = <H> = \hbar \omega \left[ n(\omega, T) + \frac{1}{2} \right]$

Energy vs. Temperature ($\omega_d = 10^{13} \text{ s}^{-1}$)

Zero point energy
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: $<E_{\text{tot}}> = k_B T$
• For a quantum harmonic oscillator, the temperature dependence is buried in the occupation number: $<E_{\text{tot}}> = \hbar \omega \left[ n(\omega, T) + \frac{1}{2} \right]$
• 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