CHM 421/621
Statistical Mechanics

Lecture 4 Energy in classical systems

Introduction and Review

Lecture Plan

Concept of Energy
- A conservation principle
- Classical single particle
- Classical *N*-particle system
- Postulate of extensivity of energy

Concept of Energy

A conservation principle

The work done in taking a (macroscopic) system between two equilibrium states through an adiabatic process is independent of the path taken.

The implied state function is termed as internal energy of the system (*U*) defined as *the capacity to do work*.

Conservation principle : Macroscopic systems have definite and precise energies subject to a definite conservation principle. (First law of ThermoD)

Concept of Energy

Classical single particle

Classical mechanics ascribes (time-varying) coordinates (**r**) and velocities (**v**) of a particle as its dynamical degrees.

$$\mathbf{v} = \frac{d\mathbf{r}}{dt}$$

$$\mathbf{F} = m\frac{d\mathbf{v}}{dt}$$ Newton's Law

$$\epsilon_{kin} = \frac{1}{2}m\mathbf{v}^2$$ Translational kinetic energy

Thus,

$$\frac{d\epsilon_{kin}}{dt} = \mathbf{v} \cdot \mathbf{F}$$

Work-Energy Theorem (Integrate over total time for which the force is applied)

Concept of Energy

Classical single particle

If ***F*** is a conservative force $\mathbf{F} = -\nabla\phi(\mathbf{r})$ then we can write

$$\frac{d\epsilon_{kin}}{dt} = \mathbf{v}\cdot\mathbf{F} = -\mathbf{v}\cdot\nabla\phi(\mathbf{r})$$

Implies

$$\frac{d}{dt}\left(\epsilon_{kin} + \phi(\mathbf{r})\right) = 0$$

The quantity

$$\epsilon = \frac{1}{2}m\mathbf{v}^2 + \phi(\mathbf{r})$$

Potential energy

is a constant of motion termed the total energy of the particle.

Hence, the total energy of the system is conserved.

Note that if non-conservative forces then $\frac{d}{dt}\left(\epsilon_{kin} + \phi(\mathbf{r})\right) = \mathbf{v}\cdot\mathbf{F}_{nc}$

Concept of Energy

Classical single particle

Simple examples.

Free particle, $\phi(\mathbf{r}) = 0$

Simple harmonic oscillator (1-d) $\phi(x) = \frac{1}{2}m\omega^2 x^2$

$$\epsilon = \frac{1}{2}mv^2 + \frac{1}{2}m\omega^2 x^2$$

Note that the absolute value of energy has no meaning but only changes in it during a process.

Concept of Energy

Classical *N*-particle system

Total kinetic energy

$$E_{kin} = \sum_{I=1}^{N} \frac{1}{2} m \mathbf{v}_i^2$$

Potential energy (assuming non-interacting particles)

$$\phi_{ext} = \sum_{I=1}^{N} \phi(\mathbf{r}_i)$$

Due to external conservative fields

Concept of Energy

Classical *N*-particle system

Inter-particle interactions

Force due to particle *j* on particle *i* is given by

$$\mathbf{F}_i = -\frac{\partial \Phi(\mathbf{r}_{ij})}{\partial \mathbf{r}_j} = -\mathbf{F}_j$$

Usually, potential only depends on the distance between the particles.
The general form of this inter-particle interaction potential is complicated.

Concept of Energy

Classical *N*-particle system

Inter-particle interactions

In many cases,

$$\Phi(\{\mathbf{r}_{ij}\}) = \frac{1}{2}\sum_{i\neq j}\phi(\mathbf{r}_{ij})$$

Where $\phi(r)$ usually goes to 0 as $r \to \infty$

Example,

$$\phi(r) = \epsilon_0\left[\left(\frac{r_0}{r}\right)^{12} - 2\left(\frac{r_0}{r}\right)^{6}\right]$$

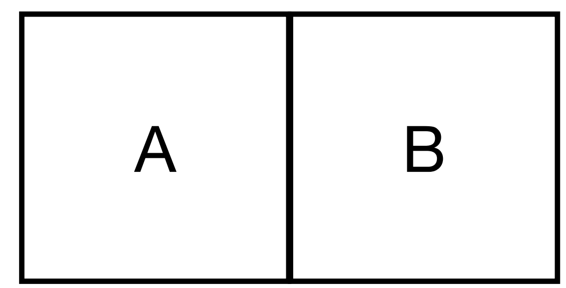
Generally, interactions are short-ranged and often depend on number of interacting neighbours in the immediate vicinity of a particle.

Concept of Energy

Postulate of extensivity of energy

We assume that the energy of a macroscopic function is an extensive function.

$$E(A+B) = E(A) + E(B)$$



$$N \sim L^3$$

$$N_s \sim L^2$$

$$E(A+B) = (\epsilon_b^A + \epsilon_b^B) \times L^3 + (\epsilon_s^A + \epsilon_s^B) \times L^2$$

$$\epsilon(A+B) = E(A+B)/V \sim (\epsilon_b^A + \epsilon_b^B) + (\epsilon_s^A + \epsilon_s^B)/L$$

$$\to \epsilon(A) + \epsilon(B) \ (L \to \infty)$$