

Part II: Thermodynamics

II.1 The first law of thermodynamics

Class schedule: Jan 27, 29

Reading assignments: S4-S5, R2.6-R2.8, R2.11, F1-3

II.1.1 Internal energy

Internal energy is the total constant energy of an isolated system, including kinetic energy of system particles and potential energy due to interactions between these particles. The amount of internal energy relative to the potential energy reference is also called *thermal energy*.

Example 1: the potential energy of an atom in a solid, a liquid, and a gas.

Example 2: energies for translational motions, rotations, and vibrations of particles.

The *degrees of freedom* is the number of different ways a particle stores thermal energy, denoted as ν , and the degrees of freedom of N particles of the same kind is $f = \nu N$.

Example 3: find the degrees of freedom of: (a) ideal monatomic gas; (b) ideal diatomic gas; (c) atoms in a solid; (d) conduction electrons in a solid; (e) a liquid

equipartition theorem: in many situations, energy is equally distributed to all degrees of freedom. Each degree of freedom has an average energy of $\frac{1}{2}kT$.

Example 4: the changes in the degrees of freedom and internal energy when a solid melts into a liquid.

Example 5: root-mean-square velocity of gas particles $v_{rms} = \sqrt{3kT/m}$.

II.1.2 Interactions

There are in general three kinds of interactions between systems: *heat transfer* or *thermal interaction*, *work* or *mechanical interaction*, and *particle transfer* or *diffusive interaction*.

Example 6: work done by pressure in a *quasi-static* process

II.1.3 The first law

The first law reflects conservation of energy.

Internal energy is a *state parameter*, and dE refers to the “real” difference between two states in equilibrium, which is determined by the initial and final states and INDEPENDENT of the path the system takes to evolve from one to another state.

Work and heat are NOT state parameters. They are the amount of energy transferred during a process. It is not a correct statement to describe a system having a certain amount of “heat” or “work”.

Mathematically, the differential of internal energy is an *exact differential*, while those of heat and work are *inexact differentials*.

Example 7: exact and inexact differentials

Only when the system evolves quasi-statically with complete thermal insulation, the amount of the work done is independent of the process and is determined by the initial and final states, i.e., the difference in the internal energy between two states. Similarly, only when the system evolves quasi-statically without any mechanical interaction, the amount of heat transfer is determined by the initial and final states.

Example 8: calculating work and heat when a system evolves from the initial to the final state along different paths.

Example 9: review: the number of microscopic states in a macroscopic system: dependence on internal energy.