

PHYS4171-Thermal Physics and Statistical Mechanics, Winter 2007

Note for Midterm #1

Thermodynamic Systems, Microstates and Macrostates

- i. Thermodynamic Systems are comprised of large number of atoms or molecules ($N > \text{mole} = 6.023 \times 10^{23}$). They can exist as a gas, liquid, or solid. For the midterm you will be concern mainly with systems in the gas states.
- ii. The Microstates of a system are specified by the microscopic parameters of the atoms and/or molecules that comprise the systems. For example, the microstates of a helium gas are specified by the positions, momenta, and energies of the helium atoms.
- iii. The Macrostates of a system are specified by macroscopic parameters that can be determined by experiments. Examples of such macroscopic parameters are the temperature (T), pressure (P), volume (V), and energy (E) of the system.

The Ideal Gas

A system of **ideal gas** is comprised atoms or molecules at sufficiently low density (dilute) to neglect the interactions between them.

- i. Ideal Gas Equation $PV = Nk_B T$
- ii. The Equipartition Theorem states that the energy of a system of ideal gas is $E = \frac{f}{2} Nk_B T$, where N is the number of particles in the system, and f is the number of active quadratic degrees of freedom.
- iii. A system of monatomic ideal gas is comprised of one kind of atoms, usually a rare gas such as helium, argon, or xenon. There are three translation degrees of freedom. Hence the energy is $E = \frac{3}{2} Nk_B T$, always.
- iv. A system of diatomic ideal gas is comprised molecules of two bonded atoms. Examples are hydrogen molecules (H_2), oxygen molecules (O_2), and carbon monoxide (CO). There are three translation, two rotational, and one vibrational degrees of freedom. Near room temperature ($\sim 300K$) only the translational and rotational degrees of freedom are active, $f = 5$, $E = \frac{5}{2} Nk_B T$, near room temperaure $\approx 300K$. At

high temperatures ($> 700\text{ K}$) all degrees of freedom are active, $f = 6$,
 $E = \frac{6}{2} N k_B T$, high temperature $> 700\text{ K}$.

- v. A system of polyatomic ideal gas is comprised molecules of three or more bonded atoms. Examples are water molecules (H_2O), carbon dioxide (CO_2), and methane (CH_4). In general, there are three translation, three rotational, and $3n - 6$ vibrational degrees of freedom, where n is the number of atoms in the polyatomic molecules.

The Multiplicity of a Macrostate of a Monatomic Ideal Gas

For a given **macrostate** (specified by T, P, V, E, \dots), there are many possible **microstates**. The number of **microstates** of a **macrostate** is the **multiplicity** of the **macrostate**.

A system of **monatomic ideal gas** with N particles in a macrostate described by the temperature, and volume, V , has the multiplicity:

$$\Omega = DV^N T^{3N/2}, \text{ where } D \text{ is a constant.}$$

The Entropy of a Macrostate of a Monatomic Ideal Gas

The **entropy** is defined as $S = k_B \ln \Omega$.

A monatomic ideal gas has the entropy

$$S = k_B \ln(DV^N T^{3N/2}), \text{ where } D \text{ is a constant.}$$

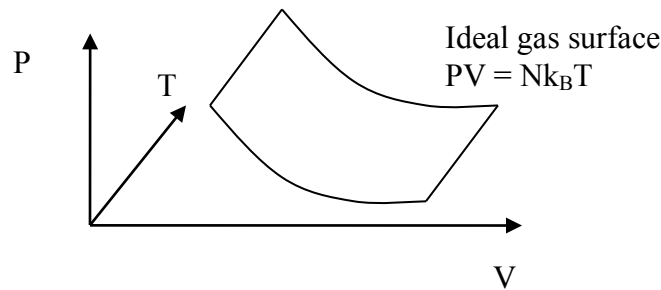
State Functions

The macrostates or thermodynamic states of a thermodynamic system are defined by state functions, also called state variables or thermodynamic functions, which are macroscopic parameters that can be determined experimentally. Thus far we have concentrated on gas systems where, the state functions (thermodynamic functions) are: temperature (T), pressure (P), volume (V), energy (E), and entropy (S). So far we have assumed that the number of particles in the gas system, N , is fixed.

Equation of State

The equilibrium states of a thermodynamic system are described by equation of states, which are mathematical relations that relate the state functions (P, V, T...). For a gas system of N particles, an equation of state of three state variables completely specifies the macrostates.

An important example is the ideal gas equation $PV = Nk_B T \rightarrow P = \frac{Nk_B T}{V}$, and consequently P is a function of T and V, which is a surface in the PVT coordinate system. The ideal gas surface is illustrated below.



However, it should be noted that the choice of the state functions P, V, T is not unique. The macrostates of a gas system can be expressed in terms of an equation of state involving any three state functions. For example, another equation of state for a monatomic ideal gas is the Sackur-Tetrode equation

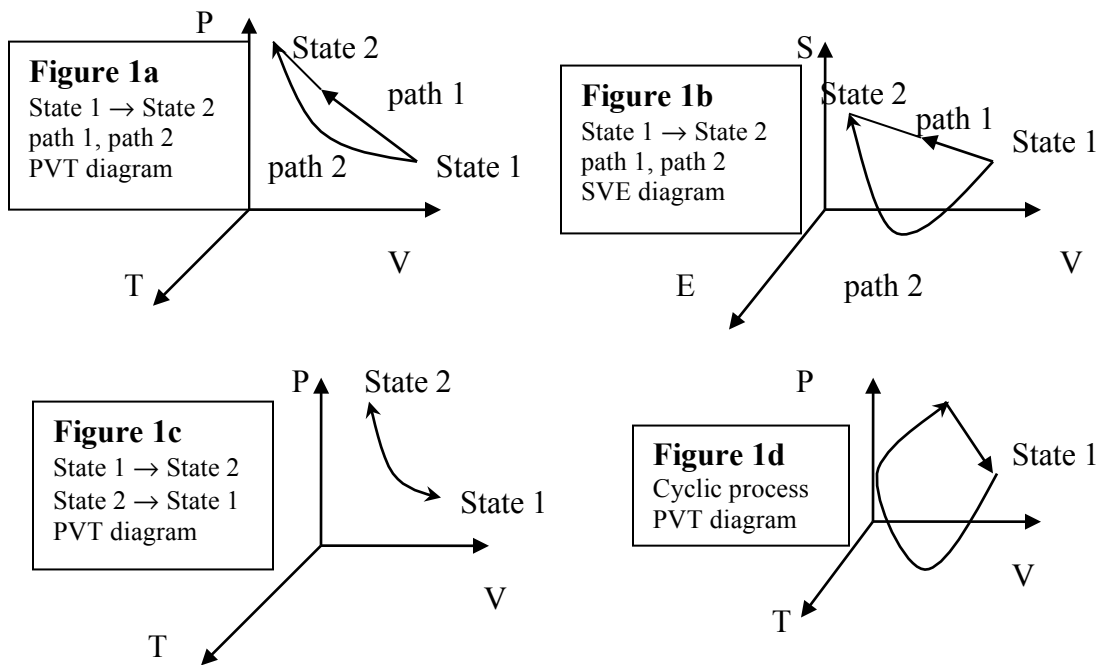
$$S = Nk_B \left[\ln \left(\frac{V}{N} \left(\frac{2\pi m E}{3Nh^2} \right)^{3/2} \right) + \frac{5}{2} \right].$$
 This equation expresses S as a function of E

and V, and is a surface in the SVE coordinate system. Later it will be shown that for a monatomic ideal gas, the ideal gas equation and the **Sackur-Tetrode** equation are equivalent.

Thermodynamic Processes and State Functions

Thermodynamics is the study of how the state functions change when a system undergoes a thermodynamic process. Examples of thermodynamic processes are an adiabatic compression of a gas and the heating of a liquid.

In a thermodynamic process, the state functions follow vary along a curve. For example, in the adiabatic compression of a gas, the variation of P, V and T are along curves (paths), as shown in figures 1a, 1c, and 1d. These curves (paths) are described by the equations $P = P(V)$, or $P = P(T)$, or $T = T(V)$. As shown in figure 1b, the variation of state functions can also be described by the equations $S = S(E)$, $S = S(V)$, or $E = E(V)$.



The change of the state functions in the thermodynamic processes shown in Figures 1a-1d depends only on the endpoints, but not the paths taken:

- i. Figure 1a: For both path 1 and path 2

$$\Delta P = P_2 - P_1, P_1 - \text{pressure in state 1}, P_2 - \text{pressure in state 2}$$

$$\Delta V = V_2 - V_1, V_1 - \text{volume in state 1}, V_2 - \text{volume in state 2}$$

$$\Delta T = T_2 - T_1, T_1 - \text{temperature in state 1}, T_2 - \text{temperature in state 2}$$

$$\Delta S = S_2 - S_1, S_1 - \text{entropy in state 1}, S_2 - \text{entropy in state 2}$$

$$\Delta E = E_2 - E_1, E_1 - \text{energy in state 1}, E_2 - \text{energy in state 2}$$

- ii. Figure 1b: $\Delta P = P_2 - P_1$, $\Delta V = V_2 - V_1$, $\Delta T = T_2 - T_1$, $\Delta S = S_2 - S_1$, and

$$\Delta E = E_2 - E_1.$$

- iii. Figure 1c: For reverse processes the change in state functions are

$$\text{negative. } \Delta P_{1 \rightarrow 2} = P_2 - P_1 = -(P_1 - P_2) = -\Delta P_{2 \rightarrow 1}, \Delta V_{1 \rightarrow 2} = -\Delta V_{2 \rightarrow 1},$$

$$\Delta T_{1 \rightarrow 2} = -\Delta T_{2 \rightarrow 1}, \Delta S_{1 \rightarrow 2} = -\Delta S_{2 \rightarrow 1}, \text{ and } \Delta E_{1 \rightarrow 2} = -\Delta E_{2 \rightarrow 1},$$

- iv. Figure 1d: For cyclic processes the state functions do not change:
 $\Delta P=0$, $\Delta V=0$, $\Delta T=0$, $\Delta S=S_2-S_1$, and $\Delta E=0$.

Work and Heat in Quasistatic (Slow) Processes, and the First Law of Thermodynamics

A thermodynamic process in which the system remains in equilibrium during the whole process is called a quasistatic or slow process. The process

In any thermodynamic process, there can be a heat flow, Q , into (out of) the system from (to) an external source (such as a heat reservoir or the surrounding environment). The system may also perform work, W , on the surrounding environment. W and Q are the way that the system exchanges energy with the surrounding environment.

In any thermodynamic process there must be conservation of energy. This is expressed by the first law of thermodynamics:

$$Q = W + \Delta E, \Delta E \text{ is the change in energy of the system.}$$

The Heat Capacity is defined as $C \equiv \frac{\text{heat flow}}{\text{change in temperature}} = \frac{Q}{\Delta T}$. For a gas

system there are two important kinds of heat capacity C_v, C_p , the heat capacity at constant volume and pressure. For an ideal gas system:

$$C_v = \frac{Nf}{2}k_B, C_p = \frac{N(f+2)}{2}k_B, \text{ where } f \text{ is the active degree of freedom. An}$$

important parameter is $\gamma = \frac{C_p}{C_v}$. For an ideal gas $\gamma = \frac{C_p}{C_v} = \frac{f+2}{f} = 1 + \frac{2}{f}$.

Quasistatic (slow) processes of a gas system:

- i. Work Done $W = \int_{V_i}^{V_f} P dV$, V_i and V_f , are the volume of the initial and final states respectively. As mentioned earlier in a thermodynamic process, the pressure is a function of the volume $P = P(V)$.
- ii. Heat Flow For an isothermal process in which temperature remains constant $Q = T\Delta S$, ΔS is the change in the entropy of the system.
- iii. For a process in which the temperature changes, use $\Delta S = \frac{q}{T}$, where q is the infinitesimal heat flow, and $q = C\Delta T$, where C is the heat capacity

and ΔT is the infinitesimal change in temperature. The total change in entropy is $\Delta S = \int_{V_i}^{V_f} \frac{C}{T} dT$.

Isothermal Compression (Expansion)

In an isothermal compression (expansion) the temperature, T , remains constant. For an ideal gas using the equipartition theorem $E = \frac{f}{2} Nk_B T$, it is easy to see that $\Delta E = 0$. Given an initial state values P_i, V_i, T the final state values P_f, V_f, T can be found by the ideal gas equation $PV = NkT$. The initial and final entropy S_i and S_f , can be found from the Sackur-Tetrode equation.

The work done is $W = \int_{V_i}^{V_f} P dV = Nk_B T \int_{V_i}^{V_f} \frac{dV}{V}$.

Adiabatic Compression (Expansion)

Here the system is insulated so that $Q = 0 \rightarrow W = -\Delta E$. For an ideal gas system it was shown in class (and in the textbook) that $TV^{\gamma-1} = \text{constant}$ and $PV^{\gamma} = \text{constant}$. Hence given an initial state values P_i, V_i, T_i the final state values P_f, V_f, T_f can be found by the equations $T_i V_i^{\gamma-1} = T_f V_f^{\gamma-1}$ and $P_i V_i^{\gamma} = P_f V_f^{\gamma}$. The initial and final entropy S_i and S_f , can be found from the Sackur-

Tetrode equation. Finally using $PV^{\gamma} = P_i V_i^{\gamma} \Rightarrow P = P_i V_i^{\gamma} \frac{1}{V^{\gamma}}$, and assuming that the process is quasistatic (slow), the work done by the system is

$W = \int_{V_i}^{V_f} P dV = P_i V_i^{\gamma} \int_{V_i}^{V_f} \frac{dV}{V^{\gamma}}$. The change in energy is found from the equation

$W = -\Delta E$.

Spontaneous (Rapid) Processes

If a thermodynamic process occurs very rapidly, the process is said to be spontaneous. Examples are the free expansion of a gas, or a very rapid compression of a gas. During these processes the gas are never in equilibrium. The following points are relevant:

- i. Just as for quasistatic (slow) process, in a spontaneous (rapid) process the change in state function P , V , T , E , and S still depends only on the endpoints of the process.
- ii. Work Done The work done by the gas is $W < \int_{V_i}^{V_f} P dV$. This differs from quasistatic (slow) process where the equality sign applies in the equation.
- iii. Entropy and Heat Flow For a isothermal process, the heat flow (Q) and change in entropy (ΔS) are related by the inequality $\Delta S > \frac{Q}{T}$. This differs from quasistatic (slow) process where the equality sign applies in the equation.

Second Law of Thermodynamics

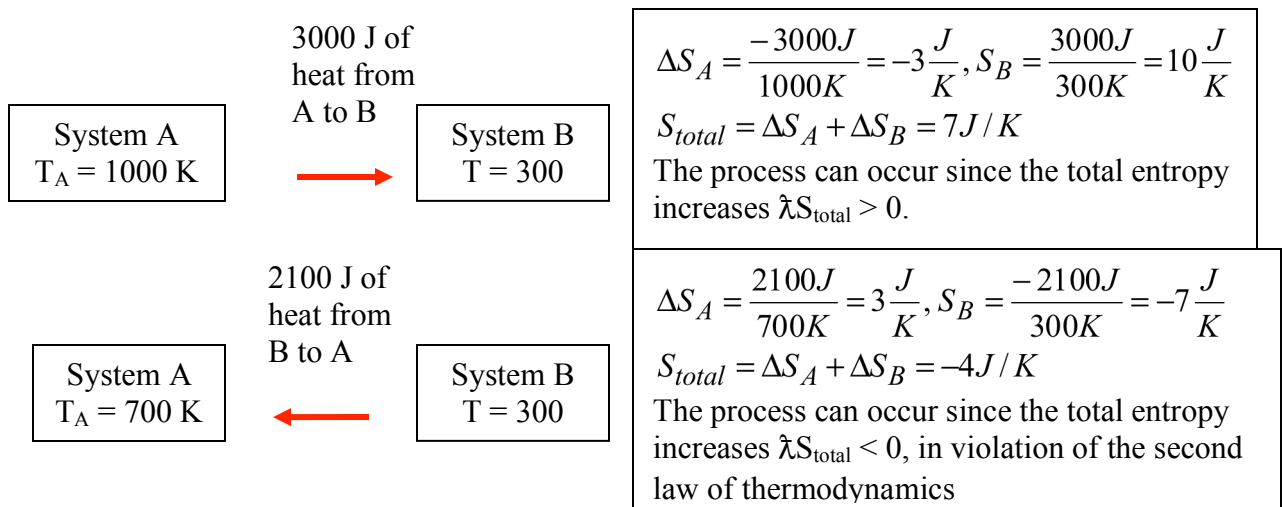
- i. First Version Consider an isolated system of many molecules whose macrostate is allowed to change. With overwhelming probability it will evolve to the macrostate with greatest multiplicity and remains there for a long time.
- ii. Second Version An isolated system will equilibrate to the macrostate (specified by P , V , T , S ...) that maximizes its entropy.
- iii. Third Version If an isolated system is allowed to change, its entropy will either remain the same or it will increase: $\Delta S \geq 0$.
- iv. Final Version If an isolated system is allowed to change, $\Delta S = 0$, for a quasistatic (slow) process, and $\Delta S > 0$, for a spontaneous (rapid) process.

Clarification of the Second Law of Thermodynamics

- i. The second law applies only to an isolated system that cannot exchange energy with its surrounding
- ii. For a system in contact with a heat reservoir, the second law applies if and only if the total change in entropy (system + reservoir) is considered.

Forbidden Processes

Process that violates the second law of thermodynamics cannot occur. Consider hypothetical systems with infinite heat capacity, $C = \infty$, which remain at the same temperatures regardless of the heat flow into or out of the systems.



Reversible and Irreversible Processes

- i. Reversible Quasistatic (Slow) Process As mention in a quasistatic process there is no change in entropy $\Delta S_{forward} = 0$. Hence the reverse process is also allowed since $\Delta S_{reverse} = -\Delta S_{forward} = 0$. It is said that the forward process is reversible. For example a slow isothermal expansion is reversible, since the reverse process, a slow isothermal expansion, would not change the total entropy (system+ environment).
- ii. Irreversible Spontaneous (Rapid) Process As mention in a spontaneous process there is no change in entropy $\Delta S_{forward} > 0$. Hence the reverse process is not allowed since $\Delta S_{reverse} = -\Delta S_{forward} < 0$, which violates the second law. It is said that the forward process is irreversible. For example a free expansion is irreversible, since the reverse process would result in an increase in entropy.

Heat Engines (Chapter 3)

- i. Efficiency The efficiency of a heat engine is

$$e = 1 - \frac{\text{heat expelled during one cycle}}{\text{heat extracted during one cycle}}.$$
 See question 1 of assignment #3.
- ii. Efficiency of a Carnot Cycle

$$e = 1 - \frac{Q_c}{Q_h} = 1 - \frac{T_h}{T_c},$$
 valid for quasistatic (slow) process. (equation 3.4 in text)

Density of State (Chapter 4) See problem 4 and 5 of assignment

Gibb's Method for finding **density of state**, which in three dimensions (3D)

is $\frac{(\text{Position Volume})(\text{Momentum Volume})}{h^3} = \frac{V}{h^3} 4\pi p^2 dp$. This then uses the free

particle dispersion relation $\varepsilon = p^2 / 2m \rightarrow d\varepsilon = 2pdp / m$ to give

$$D(\varepsilon) = \frac{2\pi(2m)^{3/2} V \varepsilon^{1/2}}{h^3} \quad (4.11)$$

Number of particle state with energy $\varepsilon = \varepsilon_1$ to $\varepsilon = \varepsilon_2$, $N_{\varepsilon_1, \varepsilon_2} = \int_{\varepsilon_1}^{\varepsilon_2} d\varepsilon D(\varepsilon)$.

Canonical Ensemble (Chapter 5) See Problem 1 and 2 of chapter 5, Problem 4 and 5 of assignment 3.

For a system in contact with a heat reservoir at temperature T , the probability that a microstate j with energy E_j is occupied is

$$P(j) = \frac{e^{-\frac{E_j}{kT}}}{Z}, \text{ where } Z_1 = \sum_i e^{-\frac{E_i}{kT}} \text{ is the one-particle partition function.}$$

Semi-classical one-particle partition $Z_1 = \int_0^\infty D(\varepsilon) \exp(-\beta\varepsilon)$

N **distinguishable** non-interacting particles, $Z_N = Z_1^N$.

N **indistinguishable** non-interacting particles, $Z_N = \frac{Z_1^N}{N!}$.

Equipartition Theorem example:

The density of state of a 3d free particle is given by $D(\varepsilon) = \frac{2\pi(2m)^{3/2} V \varepsilon^{1/2}}{h^3}$, where ε is the energy of a particle. In the canonical ensemble, at temperature T , the total number of particles is determined by $N = \int_0^\infty d\varepsilon D(\varepsilon) \exp(-\varepsilon / k_B T)$. Show $N = \left(\frac{(2\pi m)^{3/2} V}{h^3} \right) (k_B T)^{3/2}$.

The average energy at temperature, T , is $\langle E \rangle = \int_0^\infty d\varepsilon \varepsilon D(\varepsilon) \exp(-\varepsilon / k_B T)$. Show

$\langle E \rangle = \frac{(2\pi m)^{3/2} V (k_B T)^{3/2}}{h^3} \frac{3}{2} k_B T$. Use the results to determine the equipartition theorem of a monatomic ideal gas.

Solution:

$$N = \int_0^\infty d\varepsilon D(\varepsilon) \exp(-\varepsilon / k_B T) = \frac{2\pi(2m)^{3/2} V}{h^3} \int_0^\infty d\varepsilon \varepsilon^{1/2} \exp(-\varepsilon / k_B T).$$

Substitute $x^2 = \varepsilon / k_B T \rightarrow \varepsilon = k_B T x^2 \rightarrow d\varepsilon = 2k_B T x dx$, gives

$$N = 2 \frac{2\pi(2m)^{3/2} V}{h^3} (k_B T)^{3/2} \int_0^\infty dx x^2 \exp(-x^2). \text{ Use integral } \int_0^\infty x^2 \exp(-ax^2) = \sqrt{\pi} / 4a^{3/2} \text{ to}$$

$$\text{get } N = 2 \frac{2\pi(2m)^{3/2} V}{h^3} (k_B T)^{3/2} \frac{\sqrt{\pi}}{4} = \left(\frac{(2\pi m)^{3/2} V}{h^3} \right) (k_B T)^{3/2}.$$

For mean (average) energy

$$\langle E \rangle = \int_0^\infty d\varepsilon \varepsilon D(\varepsilon) \exp(-\varepsilon / k_B T) = \frac{2\pi(2m)^{3/2} V}{h^3} \int_0^\infty d\varepsilon \varepsilon^{3/2} \exp(-\varepsilon / k_B T)$$

Substitute $x^2 = \varepsilon / k_B T \rightarrow \varepsilon = k_B T x^2 \rightarrow d\varepsilon = 2k_B T x dx$ and using

$$\int_0^\infty x^4 \exp(-ax^2) = 3\sqrt{\pi} / (8a^{5/2})$$

$$\langle E \rangle = 2 \frac{2\pi(2m)^{3/2} V}{h^3} (k_B T)^{5/2} \int_0^\infty dx x^4 \exp(-x^2) = 2 \frac{2\pi(2m)^{3/2} V}{h^3} (k_B T)^{5/2} \frac{3\sqrt{\pi}}{8}$$

$$\langle E \rangle = \frac{(2\pi m)^{3/2} V (k_B T)^{3/2}}{h^3} \frac{3}{2} k_B T. \text{ Using } N = \frac{(2\pi m)^{3/2} V (k_B T)^{3/2}}{h^3} \rightarrow \langle E \rangle = \frac{3N}{2} k_B T.$$