# Resumen Física para Computación FaMAF 2017 - P3: Termodinámica

Agustín Curto

## 1 Temperature

# Summary

#### **Definitions**

- Two objects are in thermal equilibrium with each other if they do not exchange energy when in thermal contact.
- Temperature is the property that determines whether an object is in thermal equilibrium with other objects. Two objects in thermal equilibrium with each other are at the same temperature. The SI unit of absolute temperature is the **kelvin**, which is defined to be 1/273.16 of the difference between absolute zero and the temperature of the triple point of water.

#### **Concepts and Principles**

The zeroth law of thermodynamics states that if objects A and B are separately in thermal equilibrium with a third object C, then objects A and B are in thermal equilibrium with each other.

When the temperature of an object is changed by an amount  $\Delta T$ , its length changes by an amount  $\Delta L$  that is proportional to  $\Delta T$  and to its initial length  $L_i$ :

$$\Delta L = \alpha L_i \Delta T \tag{19.4}$$

where the constant  $\alpha$  is the average coefficient of linear expansion. The average coefficient of volume expansion  $\beta$  for a solid is approximately equal to  $3\alpha$ .

An ideal gas is one for which PV/nT is constant. An ideal gas is described by the equation of state,

$$PV = nRT ag{19.8}$$

where n equals the number of moles of the gas, P is its pressure, V is its volume, R is the universal gas constant (8.314 J/mol·K), and T is the absolute temperature of the gas. A real gas behaves approximately as an ideal gas if it has a low density.

# 2 The first law of thermodynamics

## **Summary**

#### **Definitions**

Internal energy is a system's energy associated with its temperature and its physical state (solid, liquid, gas). Internal energy includes kinetic energy of random translation, rotation, and vibration of molecules; vibrational potential energy within molecules; and potential energy between molecules.

**Heat** is the process of energy transfer across the boundary of a system resulting from a temperature difference between the system and its surroundings. The symbol Q represents the amount of energy transferred by this process.

A **calorie** is the amount of energy necessary to raise the temperature of 1 g of water from 14.5°C to 15.5°C.

The **heat capacity** C of any sample is the amount of energy needed to raise the temperature of the sample by 1°C.

The **specific heat** c of a substance is the heat capacity per unit mass:

$$c \equiv \frac{Q}{m \Lambda T}$$
 (20.3)

The **latent heat** of a substance is defined as the ratio of the energy input to a substance to the change in mass of the higher-phase material:

$$L \equiv \frac{Q}{\Lambda m}$$
 (20.6)

#### **Concepts and Principles**

The energy Q required to change the temperature of a mass m of a substance by an amount  $\Delta T$  is

$$Q = mc \Delta T ag{20.4}$$

where c is the specific heat of the substance.

The energy required to change the phase of a pure substance is

$$Q = L \Delta m ag{20.7}$$

where L is the latent heat of the substance, which depends on the nature of the phase change and the substance, and  $\Delta m$  is the change in mass of the higher-phase material. The work done on a gas as its volume changes from some initial value  $V_i$  to some final value  $V_f$  is

$$W = -\int_{V_i}^{V_f} P \, dV$$
 (20.9)

where P is the pressure of the gas, which may vary during the process. To evaluate W, the process must be fully specified; that is, P and V must be known during each step. The work done depends on the path taken between the initial and final states.

The **first law of thermodynamics** is a specific reduction of the conservation of energy equation (Eq. 8.2) and states that when a system undergoes a change from one state to another, the change in its internal energy is

$$\Delta E_{\rm int} = Q + W \tag{20.10}$$

where Q is the energy transferred into the system by heat and W is the work done on the system. Although Q and W both depend on the path taken from the initial state to the final state, the quantity  $\Delta E_{\rm int}$  does not depend on the path.

In a **cyclic process** (one that originates and terminates at the same state),  $\Delta E_{\rm int} = 0$  and therefore Q = -W. That is, the energy transferred into the system by heat equals the negative of the work done on the system during the process.

In an **adiabatic process**, no energy is transferred by heat between the system and its surroundings (Q=0). In this case, the first law gives  $\Delta E_{\rm int}=W$ . In the **adiabatic free expansion** of a gas, Q=0 and W=0, so  $\Delta E_{\rm int}=0$ . That is, the internal energy of the gas does not change in such a process.

An **isobaric process** is one that occurs at constant pressure. The work done on a gas in such a process is  $W = -P(V_f - V_i)$ .

An **isovolumetric process** is one that occurs at constant volume. No work is done in such a process, so  $\Delta E_{\rm int} = Q$ .

An **isothermal process** is one that occurs at constant temperature. The work done on an ideal gas during an isothermal process is

$$W = nRT \ln \left(\frac{V_i}{V_f}\right)$$
 (20.14)

**Conduction** can be viewed as an exchange of kinetic energy between colliding molecules or electrons. The rate of energy transfer by conduction through a slab of area *A* is

$$P = kA \left| \frac{dT}{dx} \right|$$
 (20.15)

where k is the **thermal conductivity** of the material from which the slab is made and |dT/dx| is the **temperature gradient.** 

In **convection**, a warm substance transfers energy from one location to another.

All objects emit **thermal radiation** in the form of electromagnetic waves at the rate

$$P = \sigma A e T^4 \qquad (20.19)$$

## 3 The kinetic theory of gases

## Summary

## **Concepts and Principles**

The pressure of N molecules of an ideal gas contained in a volume V is

$$P = \frac{2}{3} \left( \frac{N}{V} \right) (\frac{1}{2} m_0 \overline{v^2})$$
 (21.15)

The average translational kinetic energy per molecule of a gas,  $\frac{1}{2}m_0v^2$ , is related to the temperature T of the gas through the expression

$$\frac{1}{2}m_0\overline{v^2} = \frac{3}{2}k_{\rm B}T$$
 (21.19)

where  $k_B$  is Boltzmann's constant. Each translational degree of freedom (x, y, or z) has  $\frac{1}{2}k_BT$  of energy associated with it.

The molar specific heat of an ideal monatomic gas at constant volume is  $C_V = \frac{3}{2}R$ ; the molar specific heat at constant pressure is  $C_P = \frac{5}{2}R$ . The ratio of specific

heats is given by  $\gamma = C_P/C_V = \frac{5}{3}$ .

■ The **Boltzmann distribution law** describes the distribution of particles among available energy states. The relative number of particles having energy between E and E + dE is  $n_V(E)$  dE, where

$$n_V(E) = n_0 e^{-E/k_B T}$$
 (21.40)

The Maxwell–Boltzmann speed distribution function describes the distribution of speeds of molecules in a gas:

$$N_v = 4\pi N \left(\frac{m_0}{2\pi k_{\rm B}T}\right)^{3/2} v^2 e^{-m_0 v^2 / 2k_{\rm B}T}$$
 (21.41)

The internal energy of N molecules (or n mol) of an ideal monatomic gas is

$$E_{\rm int} = \frac{3}{2}Nk_{\rm B}T = \frac{3}{2}nRT$$
 (21.25)

The change in internal energy for n mol of any ideal gas that undergoes a change in temperature  $\Lambda T$  is

$$\Delta E_{\rm int} = nC_V \Delta T \tag{21.27}$$

where  $C_V$  is the molar specific heat at constant volume.

If an ideal gas undergoes an adiabatic expansion or compression, the first law of thermodynamics, together with the equation of state, shows that

$$PV^{\gamma} = \text{constant}$$
 (21.37)

Equation 21.41 enables us to calculate the **root-mean-square speed**, the **average speed**, and the **most probable speed** of molecules in a gas:

$$v_{\rm rms} = \sqrt{\overline{v^2}} = \sqrt{\frac{3k_{\rm B}T}{m_0}} = 1.73\sqrt{\frac{k_{\rm B}T}{m_0}}$$
 (21.42)

$$v_{\rm avg} = \sqrt{\frac{8k_{\rm B}T}{\pi m_0}} = 1.60 \sqrt{\frac{k_{\rm B}T}{m_0}}$$
 (21.43)

$$v_{\rm mp} = \sqrt{\frac{2k_{\rm B}T}{m_0}} = 1.41\sqrt{\frac{k_{\rm B}T}{m_0}}$$
 (21.44)

# 4 Heat engines, entropy, and the second law of thermodynamics

## Summary

## **Definitions**

The **thermal efficiency** e of a heat engine is

$$e \equiv rac{W_{
m eng}}{|Q_h|} = rac{|Q_h| - |Q_c|}{|Q_h|} = 1 - rac{|Q_c|}{|Q_h|}$$
 (22.2)

The **microstate** of a system is the description of its individual components. The **macrostate** is a description of the system from a macroscopic point of view. A given macrostate can have many microstates.

From a microscopic viewpoint, the **entropy** of a given macrostate is defined as

$$S \equiv k_{\rm B} \ln W \tag{22.10}$$

where  $k_{\rm B}$  is Boltzmann's constant and W is the number of microstates of the system corresponding to the macrostate.

In a **reversible** process, the system can be returned to its initial conditions along the same path on a *PV* diagram, and every point along this path is an equilibrium state. A process that does not satisfy these requirements is **irreversible**.

## **Concepts and Principles**

■ A **heat engine** is a device that takes in energy by heat and, operating in a cyclic process, expels a fraction of that energy by means of work. The net work done by a heat engine in carrying a working substance through a cyclic process ( $\Delta E_{\rm int} = 0$ ) is

$$W_{\rm eng} = |Q_h| - |Q_c|$$
 (22.1)

where  $|Q_h|$  is the energy taken in from a hot reservoir and  $|Q_c|$  is the energy expelled to a cold reservoir.

**Carnot's theorem** states that no real heat engine operating (irreversibly) between the temperatures  $T_c$  and  $T_h$  can be more efficient than an engine operating reversibly in a Carnot cycle between the same two temperatures.

- Two ways the **second law of thermodynamics** can be stated are as follows:
- It is impossible to construct a heat engine that, operating in a cycle, produces no effect other than the input of energy by heat from a reservoir and the performance of an equal amount of work (the Kelvin–Planck statement).
- It is impossible to construct a cyclical machine whose sole effect is to transfer energy continuously by heat from one object to another object at a higher temperature without the input of energy by work (the Clausius statement).
- The thermal efficiency of a heat engine operating in the Carnot cycle is

$$e_{\rm C} = 1 - \frac{T_c}{T_h}$$
 (22.8)

The macroscopic state of a system that has a large number of microstates has four qualities that are all related: (1) uncertainty: because of the large number of microstates, there is a large uncertainty as to which one actually exists; (2) choice: again because of the large number of microstates, there is a large number of choices from which to select as to which one exists; (3) probability: a macrostate with a large number of microstates is more likely to exist than one with a small number of microstates; (4) missing information: because of the large number of microstates, there is a high amount of missing information as to which one exists. For a thermodynamic system, all four of these can be related to the state variable of entropy.

- The second law of thermodynamics states that when real (irreversible) processes occur, there is a spatial spreading of energy. This spreading of energy is related to a thermodynamic state variable called **entropy** *S*. Therefore, yet another way the second law can be stated is as follows:
- The entropy of the Universe increases in all real processes.

lacktrianglet The **change in entropy** dS of a system during a process between two infinitesimally separated equilibrium states is

$$dS = \frac{dQ_r}{T}$$
 (22.12)

where  $dQ_r$  is the energy transfer by heat for the system for a reversible process that connects the initial and final states.

The change in entropy of a system during an arbitrary finite process between an initial state and a final state is

$$\Delta S = \int_{i}^{f} \frac{dQ_r}{T}$$
 (22.13)

The value of  $\Delta S$  for the system is the same for all paths connecting the initial and final states. The change in entropy for a system undergoing any reversible, cyclic process is zero.