Kinetic Theory and Thermodynamics

Handout 5: Introductory thermodynamics

Thermodynamical definitions

System = whatever part of the Universe we select.

Open systems can exchange particles with their surroundings. **Closed** systems cannot.

An **isolated** system is not influenced from outside its boundaries.

Adiathermal = without flow of heat. A system bounded by adiathermal walls is **thermally isolated**. Any work done on such a system produces adiathermal change.

Diathermal walls allow flow of heat. Two systems separated by diathermal walls are said to be **in thermal contact**.

Adiabatic = adiathermal and reversible [– often used synonymously with adiathermal].

Put a system in thermal contact with some new surroundings. Heat flows and/or work is done. Eventually no further change takes place: the system is said to be in a state of **thermal equilibrium**.

A **quasistatic** process is one carried out so slowly that the system passes throughout by a series of equilibrium states so is always in equilibrium. A process which is quasistatic and has no hysteresis is said to be **reversible**.

Zeroth law of thermodynamics: "two systems, each separately in thermal equilibrium with a third, are in equilibrium with each other."

A briefer statement of this law is: "thermometers work".

This allows a scale of temperature to be defined. A system has temperature T if it can maintain thermal equilibrium with an ideal gas at that temperature.

Thermodynamic state: a system is in a "thermodynamic state" if macroscopic observable properties have fixed, definite values, independent of 'how you got there'. These properties are **variables of state** or **functions of state**. Examples are volume, pressure, temperature etc. In thermal equilibrium these variables of state have no time dependence.

Functions of state can be:
(a) **extensive** (proportional to system size) e.g. energy, volume, magnetization, mass
(b) **intensive** (independent of system size) e.g. temperature, pressure, magnetic field, density

Not functions of state: position of particle numbered 4325667, total work done on a system, total heat put into the system.

(You can get to the same final thermodynamic state by different combinations of working and heating, e.g. you can end up with warm hands by rubbing them together [using the muscles in your arms to do work on them] or putting them in a toaster [adding heat - NB not advisable].)

Equations of state

In general can find an **equation of state** which connects funtcions of state: for a gas this takes the form $f(p, V, T) = 0$. An example is the equation of state for an ideal gas: $pV = nRT$.

Partial derivatives

Consider x as a function of two variables y and z. This can be written $x = x(y,z)$ and we have that

$$\mathrm{d}x = \left(\frac{\partial x}{\partial y}\right)_z \mathrm{d}y + \left(\frac{\partial x}{\partial z}\right)_y \mathrm{d}z. \tag{1}$$

But rearranging $x = x(y,z)$ can lead to having z as a function of x and y so that $z = z(x,y)$ in which case

$$\mathrm{d}z = \left(\frac{\partial z}{\partial x}\right)_y \mathrm{d}x + \left(\frac{\partial z}{\partial y}\right)_x \mathrm{d}y. \tag{2}$$

Substituting 2 into 1 gives

$$\mathrm{d}x = \left(\frac{\partial x}{\partial z}\right)_y \left(\frac{\partial z}{\partial x}\right)_y \mathrm{d}x + \left[\left(\frac{\partial x}{\partial y}\right)_z + \left(\frac{\partial x}{\partial z}\right)_y \left(\frac{\partial z}{\partial y}\right)_x\right] \mathrm{d}y.$$

The terms multiplying $\mathrm{d}x$ give the **reciprocal theorem**

$$\boxed{\left(\frac{\partial x}{\partial z}\right)_y = \frac{1}{\left(\frac{\partial z}{\partial x}\right)_y}}$$

and the terms multiplying $\mathrm{d}z$ give the **reciprocity theorem**

$$\boxed{\left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial z}\right)_x \left(\frac{\partial z}{\partial x}\right)_y = -1.}$$

Exact differentials

An expression such as $F_1(x,y)\,\mathrm{d}x + F_2(x,y)\,\mathrm{d}y$ is known as an **exact differential** if it can be written as the differential

$$\mathrm{d}f = \left(\frac{\partial f}{\partial x}\right) \mathrm{d}x + \left(\frac{\partial f}{\partial y}\right) \mathrm{d}y,$$

of a differentiable single-valued function $f(x,y)$. This implies that

$$F_1 = \left(\frac{\partial f}{\partial x}\right) \qquad F_2 = \left(\frac{\partial f}{\partial y}\right),$$

or in vector form $\mathbf{F} = \nabla f$. Hence the integral of an exact differential is path-independent so that [where 1 and 2 are shorthands for (x_1, y_1) and (x_2, y_2)]

$$\int_1^2 F_1(x,y)\,\mathrm{d}x + F_2(x,y)\,\mathrm{d}y = \int_1^2 \mathbf{F}\cdot\mathrm{d}\mathbf{r} = \int_1^2 \mathrm{d}f = f(2) - f(1),$$

and the answer depends only on the initial and final states of the system. For an **inexact differential** this is not true and knowledge of the initial and final states is not sufficient to evaluate the integral: you have to know which path was taken.

For an exact differential the integral round a closed loop is zero:

$$\oint F_1(x,y)\,\mathrm{d}x + F_2(x,y)\,\mathrm{d}y = \oint \mathbf{F}\cdot\mathrm{d}\mathbf{r} = \oint \mathrm{d}f = 0,$$

which implies $\nabla \times \mathbf{F} = 0$ (by Stokes' theorem) and hence

$$\left(\frac{\partial F_2}{\partial x}\right) = \left(\frac{\partial F_1}{\partial y}\right) \quad \text{or} \quad \left(\frac{\partial^2 f}{\partial x \partial y}\right) = \left(\frac{\partial^2 f}{\partial y \partial x}\right).$$

Functions of state have exact differentials with respect to each other.

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