
Kinetic Theory and Thermodynamics

Handout 1:

Kinetic theory and thermodynamics is your first introduction to *thermal physics*, a part of the course which also includes statistical physics (covered next term). Thermal physics arises from thinking about the behaviour of large numbers of atoms and molecules. The basic ideas in this subject are at the root of fields as diverse as statistical physics, random and stochastic processes, vacuum technology, engine design, financial markets, condensed matter physics, astrophysics and atmospheric physics. The lectures are aimed at introducing techniques for thinking about and manipulating probability distributions, providing the fundamentals of thermal physics and illustrating this material with many applications. The origins of the subject seem at first to be historically remote (with what seems like an unhealthy obsession with steam engines) but the concepts involved are profound, far-reaching and extraordinarily beautiful.

Synopsis of course (as it appears in the syllabus)

Kinetic Theory: Maxwell distribution of velocities: derivation assuming the Boltzmann factor, calculation of averages, experimental verification. Derivation of pressure and effusion formulae, distribution of velocities in an effusing beam, simple kinetic theory expressions for mean free path, thermal conductivity and viscosity; dependence on temperature and pressure, limits of validity. Practical applications of kinetic theory.

Heat transport: Conduction, radiation and convection as heat-transport mechanisms. The approximation that heat flux is proportional to the temperature gradient. Derivation of the heat diffusion equation. Generalization to systems in which heat is generated at a steady rate per unit volume. Solution by separation of variables for problems with spherical and planar symmetry. Steady-state problems, initial-value problems, and problems involving sinusoidally varying surface temperatures.

Thermodynamics: Zeroth & First laws. Heat, work and internal energy: the concept of a function of state. Slow changes and the connection with statistical mechanics: entropy and pressure as functions of state. Heat engines: Kelvin's statement of the second law of thermodynamics and the equivalence and superiority of reversible engines. The significance of $\oint dQ/T = 0$ and the fact that entropy is a function of state. Practical realization of the thermodynamic temperature scale. Entropy as $dQ_{reversible}/T$. Enthalpy, Helmholtz energy and Gibbs energy as functions of state. Maxwell relations. Concept of the equation of state; thermodynamic implications. Ideal gas, van der Waals gas. Reversible and free expansion of gas; changes in internal energy and entropy in ideal and non-ideal cases. Joule-Kelvin expansion; inversion temperature and microscopic reason for cooling. Impossibility of global entropy decreasing: connection to latent heat in phase changes. Constancy of global entropy during fluctuations around equilibrium (non-examinable). Chemical potential and its relation to Gibbs energy. Equality of chemical potential between phases in equilibrium. Latent heat and the concepts of first-order and continuous phase changes. Clausius-Clapeyron equation and simple applications. Simple practical examples of the use of thermodynamics.

Plan of the lectures

- *Week 1:* Probability distributions, Boltzmann (canonical) distribution, Maxwell-Boltzmann distribution of velocities. $p = \frac{1}{3}nm\langle v^2 \rangle$ and the ideal gas law.
- *Week 2:* Molecular effusion, transport properties (thermal conductivity, viscosity, diffusion). Thermal waves and diffusion. Solution of heat transport equation and steady-state problems.
- *Week 3:* Zeroth and first laws. Heat, work and internal energy: the concept of a function of state. Entropy and pressure as functions of state. Heat engines: Kelvin's statement of the second law of thermodynamics and the equivalence and superiority of reversible engines. Entropy as dQ_{rev}/T .
- *Week 4:* Enthalpy, Helmholtz and Gibbs energy as functions of state. Maxwell relations. Thermal radiation.
- *Week 5:* Concept of the equation of state; thermodynamic implications. Ideal gas, van der Waals gas. Reversible and free expansion of gas and changes in internal energy and entropy. Joule-Kelvin expansion; inversion temperature and microscopic reason for cooling.
- *Week 6:* Other simple thermal systems. Latent heat in phase changes.
- *Weeks 7 and 8:* Chemical potential and its relation to Gibbs function. Equality of chemical potential between phases in equilibrium. Latent heat and the concepts of first-order and continuous phase changes. Clausius-Clapeyron equation and simple applications. Third law of thermodynamics. Examples of solved problems.

Books

Consult your tutor for recommendations, but good treatments may be found in the following:

- Concepts in thermal physics: S. J. Blundell and K. M. Blundell (OUP, 2006)
(this book has been designed to cover the relevant material for the Oxford courses on kinetic theory, thermodynamics and statistical mechanics, plus some applications in astrophysics, atmospheric physics, atomic physics and condensed matter physics)
- Equilibrium thermodynamics: C. J. Adkins (CUP, 1983)
(the old war-horse contains no kinetic theory but is very sound on classical thermodynamics)
- Fundamentals of Statistical and Thermal Physics: F. Reif (McGraw Hill, 1965)
(read chapters 1 and 2 for an introduction to kinetic theory and thermal physics – the book is probably better for statistical mechanics)
- Thermal Physics: R. Baierlein (CUP, 1999)
(a good read and some very nice insights)
- Theoretical concepts in physics: M. S. Longair (second edition, CUP, 2003)
(a stimulating book on lots of topics, but for this course read chapters 9 and 10, and possibly 11–13).
- Lectures in Physics: R. P. Feynman (Addison Wesley, 1970).
(always entertaining, see Vol I, chapters 44–46 for thermodynamics)

Some useful constants

Boltzmann's constant	k_B	$1.3807 \times 10^{-23} \text{ J K}^{-1}$
Proton rest mass	m_p	$1.6726 \times 10^{-27} \text{ kg}$
Avogadro's number	N_A	$6.022 \times 10^{23} \text{ mol}^{-1}$
Standard molar volume		$22.414 \times 10^{-3} \text{ m}^3 \text{ mol}^{-1}$
Molar gas constant	R	$8.315 \text{ J mol}^{-1} \text{ K}^{-1}$

What is a mole?

A small burrowing animal, but also a name (first coined about a century ago from the German 'Molekül' [molecule]) representing a certain numerical quantity of stuff. It functions in the same way as words like 'dozen' is used to describe a certain number of eggs (12) or 'score' is used to describe a certain number of years (20). It might be easier if we could use the word dozen when describing a certain number of atoms, but a dozen atoms is not many (unless you are building a quantum computer) and since a million, a billion, and even a quadrillion are also too small to be useful, we have ended up with using an even bigger number. Unfortunately it isn't a power of ten.

The mole is *defined* as

the quantity of matter that contains as many objects (for example, atoms, molecules, formula units, ions) as the number of atoms in exactly 12 g (=0.012 kg) of ^{12}C .

This quantity is known as the **Avogadro number** N_A and is expressed to 4 significant figures as 6.022×10^{23} . (As a shorthand, I often write this as $6.022 \times 10^{23} \text{ mol}^{-1}$ to remind me of its definition, but N_A is dimensionless, as are moles. They are both numbers. By the same logic I suppose I would have to define the 'eggbox number' as 12 dozen^{-1} .)

So 1 mole of carbon is 6.022×10^{23} atoms of carbon, 1 mole of benzene is 6.022×10^{23} molecules of benzene, 1 mole of NaCl contains 6.022×10^{23} NaCl formula units, etc etc.

The molar mass is the mass of one mole of the substance. Thus the molar mass of carbon is 12 g, but the molar mass of water is close to 18 g (because the mass of a water molecule is about $\frac{18}{12}$ times larger than the mass of a carbon atom).

The mass of a single molecule or atom is therefore the molar mass of that substance *divided* by the Avogadro number.

Mathematical Preliminary

We will begin the course with Kinetic theory. Problems in kinetic theory often end up using some standard integrals which are worth memorising since they also crop up in quantum mechanics, atomic physics, statistical mechanics and many other fields.

(1) The factorial function

$$n! = \int_0^{\infty} x^n e^{-x} dx$$

- This integral is simple to prove by induction. Show that it is true for the case $n = 0$. Then assume it is true for $n = k$ and prove it is true for $n = k + 1$ (hint: integrate $(k + 1)! = \int_0^\infty x^{k+1}e^{-x} dx$ by parts.)
- It allows you to *define* the factorial of non-integer numbers. This is so useful that the integral is given a special name, the *gamma function*. However, the traditional definition of the gamma function is $\Gamma(n) = \int_0^\infty x^{n-1}e^{-x} dx$ so that $\Gamma(n) = (n - 1)!$ i.e. the factorial function and the gamma function are ‘out of step’ with each other, a rather confusing feature. In this course we will not refer again to the gamma function, but the integral will be used repeatedly. Commit it to memory.

(2) The Gaussian integral

$$\boxed{\int_{-\infty}^{\infty} e^{-\alpha x^2} dx = \sqrt{\frac{\pi}{\alpha}}}$$

- This integral was derived in the first-year
- The fun begins when we employ a cunning stratagem: we differentiate both sides of the equation with respect to α . Because x does not depend on α , this is easy to do. Hence $(d/d\alpha)e^{-\alpha x^2} = -x^2e^{-\alpha x^2}$ and $(d/d\alpha)\sqrt{\pi/\alpha} = -\sqrt{\pi}/2\alpha^{3/2}$ so that

$$\boxed{\int_{-\infty}^{\infty} x^2 e^{-\alpha x^2} dx = \frac{1}{2} \sqrt{\frac{\pi}{\alpha^3}}}$$

- This trick can be repeated with equal ease. Differentiating again gives

$$\boxed{\int_{-\infty}^{\infty} x^4 e^{-\alpha x^2} dx = \frac{3}{4} \sqrt{\frac{\pi}{\alpha^5}}}$$

- Therefore we have a way of generating the integrals between $-\infty$ and ∞ of $x^{2n}e^{-\alpha x^2}$ where $n \geq 0$ is an integer. Because these functions are even, the integrals of the same functions between 0 and ∞ are just *half* of these results:

$$\int_0^\infty e^{-\alpha x^2} dx = \frac{1}{2} \sqrt{\frac{\pi}{\alpha}}, \quad \int_0^\infty x^2 e^{-\alpha x^2} dx = \frac{1}{4} \sqrt{\frac{\pi}{\alpha^3}}, \quad \int_0^\infty x^4 e^{-\alpha x^2} dx = \frac{3}{8} \sqrt{\frac{\pi}{\alpha^5}}.$$

- To integrate $x^{2n+1}e^{-\alpha x^2}$ between $-\infty$ and ∞ is easy: the functions are all odd and so the integrals are all zero. To integrate between 0 and ∞ , start off with $\int_0^\infty x e^{-\alpha x^2} dx$ which can be done by noticing that $x e^{-\alpha x^2}$ is almost what you get when you differentiate $e^{-\alpha x^2}$. All the odd powers of x can now be obtained by differentiating that integral with respect to α .
- (Note: Another method of getting these integrals is to make the substitution $y = \alpha x^2$ and turn them into the factorial integrals considered above. This is all very well, but you need to know things like $(-\frac{1}{2})! = \sqrt{\pi}$ to get anywhere.)