Key Maths and Physics
for Statistical Mechanics

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1 Introduction

This handout summarises the key mathematical tools (Sections 2-4) and physical ideas (Sections 5-6) that you need for my third-year course 'Statistical Mechanics'. They are all from your previous mathematics and physics courses.

All this material is fairly basic, but **you need to have it at your fingertips** and be ready to apply it without a moment's hesitation. If that's not yet the case, I advise you to use your notes and textbooks from the relevant previous courses to get up to speed on this material before it's used in my course.

I'd welcome suggestions for changes or additions to future versions of this handout. And – as always in this course – don't hesitate to ask me for help if you need it.

2 Elementary Mathematics

2.1 Powers of x like x^{-2}

Ensure you can sketch a graph of, say, x^{-2} and know that it goes to infinity as x approaches zero, and goes gradually to zero as x becomes large.

2.2 Exponential functions like e^{-ax}

Ensure you can sketch a graph of e^{-ax} and know that it goes *rapidly* to zero as x becomes large.

2.3 Gaussian functions like e^{-ax^2}

Ensure you can sketch a graph of e^{-ax^2} and know that it goes *even more* rapidly to zero as x becomes large.

2.4 Taylor series (including Maclaurin and binomial series)

- Taylor expansion of the exponential function: $e^x \approx 1 + x$ for $|x| \ll 1$
- Binomial expansion of $(1 + x)^n$: $\frac{1}{1+x} \approx 1 - x$ for $|x| \ll 1$

2.5 "Pokémon law"

Very often we will come across a function which is a product of two terms, one of which goes to zero, and the other of which goes to infinity, i.e. $0 \times \infty$, requiring careful analysis. The "Pokémon law", which helps us in such cases, is my informal name for the fact that, as $x \to \infty$,

- e^{-x} falls to zero more rapidly than x^n rises to infinity, so that their product $e^{-x}\, x^n \to 0$, i.e. the exponential "wins"
- x^{-n} falls to zero more rapidly than $\ln x$ rises to infinity, so that their product $x^{-n}\, \ln x \to 0$, i.e. the power "wins"
- In short, **exponentials beat powers, and powers beat logs**.

2.6 More challenging exercises in curve sketching

Try sketching the following curves, all of which are important in statistical mechanics. (In each case, you may assume that symbols other than the one being varied are positive constants.)

(a) $c^2 e^{-mc^2/2kT}$ as a function of c from 0 to ∞;

(b) $\frac{1}{2}\hbar\omega + \dfrac{\hbar\omega}{e^{\hbar\omega/kT} - 1}$ as a function of T from 0 to ∞ (taking particular care for high T);

(c) $\dfrac{1}{e^{(\epsilon-\mu)/kT} + 1}$ as a function of ϵ from $-\infty$ to ∞;

(d) $\dfrac{1}{e^{(\epsilon-\mu)/kT} - 1}$ as a function of ϵ from μ to ∞.

2.7 Sum of geometric series

$a + ar + ar^2 + ar^3 + ar^4 + ... = \dfrac{a}{1-r}$, provided that $|r| < 1$

3 Calculus

3.1 Differentiation of basic functions

Ensure you can differentiate x^n, e^x, $\ln x$, $\sin x$, $\cos x$, both on their own, and in combinations (making use of the chain rule below).

3.2 Chain rule of differentiation

When differentiating, we will frequently use the fact that

$$\frac{dy}{dx} = \frac{dy}{du}\frac{du}{dx}.$$

E.g.

$$\frac{d}{dx}(\ln(\sin x)) = \frac{1}{\sin x}.\cos x = \cot x$$

and

$$\frac{d}{dx}(e^{-x^2}) = e^{-x^2}.(-2x) = -2xe^{-x^2}$$

3.3 Product rule of differentiation

$$\frac{d}{dx}\left(u(x)\,v(x)\right) = u\,\frac{dv}{dx} + \frac{du}{dx}\,v$$

E.g.

$$\frac{d}{dx}\left(x^2 e^{-x}\right) = 2xe^{-x} + x^2(-e^{-x}) = (2x - x^2)e^{-x}$$

3.4 Integration by change of variable

The idea is to rewrite a problematic integral in terms of a new variable of integration, such that the new integral can be performed (or looked up in tables). E.g.

$$\int\limits_{q=0}^{\infty} \frac{q^4 e^{\hbar c q/kT}}{(e^{\hbar c q/kT}-1)^2}\,dq = \int\limits_{x=0}^{\infty} \left(\frac{kTx}{\hbar c}\right)^4 \frac{e^x}{(e^x-1)^2}\left(\frac{kT\,dx}{\hbar c}\right) = \left(\frac{kT}{\hbar c}\right)^5 \left[\int\limits_{0}^{\infty} \frac{x^4 e^x}{(e^x-1)^2}dx\right] = \left(\frac{kT}{\hbar c}\right)^5 \frac{4\pi^4}{15}$$

where we choose to write $x = \frac{\hbar c}{kT}\,q$ and thus $dx = \frac{\hbar c}{kT}\,dq$, and the final step makes use of a standard integral from tables.

3.5 Three-dimensional integrals in spherical polars

If a function f happens to be a spherically symmetric function of position (i.e. f depends on r only, not θ or ϕ) then

$$\int\limits_{\text{all space}} f(r)\,dV = \int\limits_{r=0}^{\infty} f(r)\,4\pi r^2 dr$$

(the $4\pi r^2 dr$ can be thought of as the volume of a thin spherical shell).

3.6 Your table of mathematical formulae

Your official departmental table of mathematical formulae (that you should all be familiar with, since a copy will be provided to you in exams) contains many useful results related to calculus that can save you a lot of time. Be sure that you are ready to make best use of it. Results relevant to statistical mechanics include

- Gaussian definite integrals of the form $\int_0^\infty x^n\,e^{-ax^2}\,dx$
- Specific exponential definite integrals like $\int_0^\infty \frac{x^3}{e^x-1}\,dx$
- Many indefinite integrals

The table may be downloaded from `https://www.york.ac.uk/physics/internal/learning/assess/pastexampapers/`

4 Probability and Statistics

4.1 Equally-likely elementary outcomes

If a fair coin is tossed three times, each of the eight possible outcomes (HHH, HHT, HTH, HTT, THH, THT, TTH, TTT) is clearly equally likely, and so has a probability of $\frac{1}{8}$. The probability of getting two heads and a tail is therefore $\frac{3}{8}$, since three of these eight outcomes fit that description.

4.2 Permutations

A permutation is an *ordered* arrangement of objects (i.e. the same objects in a different order count as a separate permutation). The number of permutations of N distinguishable objects is the factorial $N!$ (since there are N ways of selecting the first object, then $N-1$ ways of selecting the second, etc.).

If some of the objects are indistinguishable, the expression $N!$ is larger than it should be. For each group of identical objects, we must undo the overcounting of permutations, by dividing by the number of permutations of those identical objects *among themselves*. E.g. the number of permutations of 3 identical red Smarties and 2 identical yellow Smarties is

$$\frac{5!}{3!\,2!} = 10\ .$$

4.3 Stirling's approximation for $N!$

For N large, $\ln(N!) \approx N\,\ln N - N$.

4.4 Probability distribution functions

If $f(x)$ is the probability distribution function for a random variable x, then $f(x)\,dx$ gives the probability that the variable's value is between x and $x + dx$. It follows that

- the total area $\int_{-\infty}^{\infty} f(x)\,dx$ is equal to 1
- the mean value of x is given by $\overline{x} = \int_{-\infty}^{\infty} x f(x)\,dx$
- the mean value of x^2 is given by $\overline{x^2} = \int_{-\infty}^{\infty} x^2 f(x)\,dx$

5 Quantum Mechanics

5.1 Schrödinger equation

In quantum mechanics, the possible energies of a system are given by the various values[1] of ϵ (each one accompanied by a wavefunction ψ) that satisfy the (time-independent) Schrödinger equation, which for a one-particle system takes the form

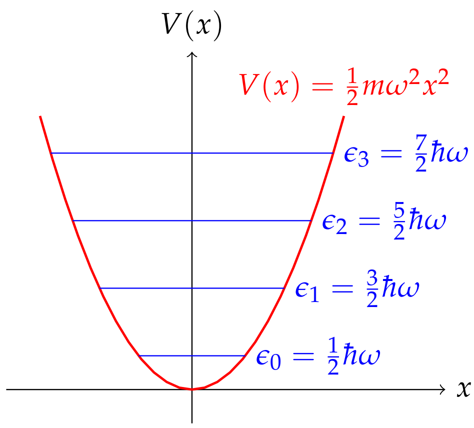
[1] I write ϵ rather than E here because our actual use of the Schrödinger equation will generally be for single-particle systems, and I prefer to reserve the symbol E for the total energy of the *overall* system of many particles.

$$-\frac{\hbar^2}{2m}\nabla^2\psi(\mathbf{r}) + V(\mathbf{r})\,\psi(\mathbf{r}) = \epsilon\,\psi(\mathbf{r})\,,$$

where $V(\mathbf{r})$ (often called "the potential" for short) is the potential energy of the particle at $\mathbf{r}$.

5.2 Harmonic oscillator

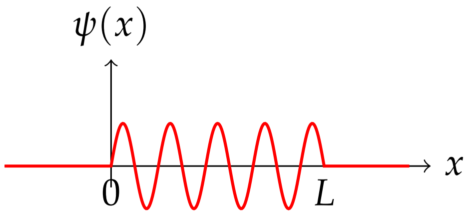
The one-dimensional simple harmonic oscillator is a familiar and important system in both classical mechanics and quantum mechanics. It is defined by the potential $V(x) = \frac{1}{2}m\omega^2x^2$ (which in classical mechanics yields the equation of simple harmonic motion $m\ddot{x} = -dV/dx = -m\omega^2 x$, reminding us that ω is the angular frequency of the oscillator). In quantum mechanics the possible energies ϵ which satisfy the Schrödinger equation are given by $\epsilon_n = (n+\frac{1}{2})\hbar\omega$, where $n = 0, 1, 2, 3, \ldots$.



5.3 Particle in a box

We will need only the well-known case of a square-well potential with infinitely high walls, so that the potential is 0 between $x = 0$ and $x = L$, and ∞ elsewhere[2]. In one dimension the solutions of the Schrödinger equation are

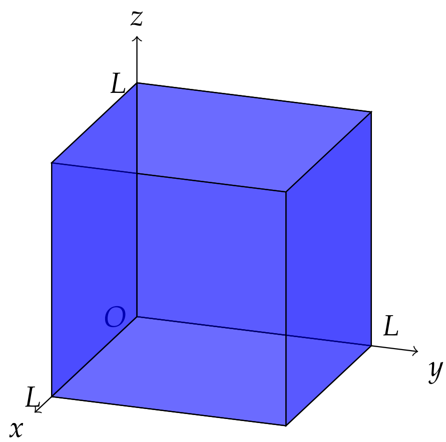
$$\epsilon = \frac{\hbar^2q^2}{2m}, \quad \psi(x) = \begin{cases} A\sin qx, & 0 \le x \le L \\ 0, & \text{otherwise} \end{cases}$$



where the wavevector[3] q is a positive integer times π/L and A is a normalisation constant. (The Figure illustrates the state with $q = 9\pi/L$.)

In three dimensions (where the box is a cube $L\times L\times L$), the method of separation of variables may be used, together with the above analysis of the one-dimensional problem, to obtain

$$\epsilon = \frac{\hbar^2q^2}{2m}, \quad \psi(\mathbf{r}) = \begin{cases} A\,\sin q_x x\,\sin q_y y\,\sin q_z z, & \text{inside box} \\ 0, & \text{outside box} \end{cases}$$



where q_x, q_y and q_z are the three components of the wavevector $\mathbf{q}$, each one a positive integer times π/L, and $q^2 = q_x^2 + q_y^2 + q_z^2$.

[2]Caution: in your quantum mechanics courses you probably analysed a well running from $x = -a$ to $x = a$, so my L is $2a$, and the shifted origin of x makes all my wavefunctions sines rather than alternating cosines and sines.

[3]I use q rather than k for wavevector in this course to avoid confusion with Boltzmann's constant.

6 Miscellaneous Physics

6.1 Phonons

Phonons are vibrational waves in a crystalline solid, in which the atoms vibrate about their equilibrium positions with an angular frequency ω, which depends on the wavevector $\mathbf{q}$ of the mode. For each wavevector $\mathbf{q}$ there are multiple phonon modes, each with a different ω: in the simplest case of a crystal with one atom per unit cell there are three modes (one longitudinal and two transverse) for each $\mathbf{q}$. It is convenient to characterise the phonons through the *dispersion relation* $\omega(\mathbf{q})$. In a crystal of size $L \times L \times L$, the allowed wavevectors $\mathbf{q}$ are exactly the same[4] as for the quantum-mechanical "particle in a box" problem above.

6.2 Electromagnetic waves in a vacuum

Electromagnetic waves in a vacuum travel with a fixed speed c, so that $\omega = cq$. For each wavevector $\mathbf{q}$ there are two modes (with the same ω), corresponding to the two possible directions of polarisation of the electric field perpendicular to $\mathbf{q}$. In a box of size $L \times L \times L$, the allowed wavevectors $\mathbf{q}$ are exactly the same as for the quantum-mechanical "particle in a box" problem above.

6.3 Thermodynamics

One of the achievements of statistical mechanics is to place the theory of thermodynamics on a secure fundamental footing based on quantum mechanics, so you will, I hope, notice all the ideas of thermodynamics (including the "laws" of thermodynamics themselves) emerging from statistical mechanics. It is, therefore, helpful to have the ideas of thermodynamics in your mind as you think about statistical mechanics.

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[4] I use the "zero" boundary conditions generally used in statistical mechanics, but it may be noted that the alternative ("periodic") boundary conditions conventional in solid-state physics allow both positive *and* negative values of q_x, etc., while doubling their spacing; this affects some intermediate details of calculations of properties of a crystal, but not the final answers.