Statistical Mechanics: Course Summary

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Introduction

This guide accompanies my Year 3 course "*Statistical Mechanics*". It is a summary of the main results which is intended to

- emphasise which results are more fundamental[1] or are applications of especially wide significance;
- reiterate the structure of the course;
- provide a convenient reference to earlier results when learning the later parts of the course or doing problems.

It is *not* a comprehensive description of the course, and should not be taken to imply which material is examinable. Equally, it is not a list of results that have to be memorised: many of the results here may (with practice) be derived quite easily from a small number of the most fundamental principles.

It is not intended to be a self-contained document. For example, the definitions of some symbols and quantities are not given (but are, of course, to be found in your lecture notes or a textbook).

When using this guide you may find it helpful to have the companion guide "*Key Maths and Physics for Statistical Mechanics*" also at hand, which sets out the most important maths and physics knowledge from your *prior* study that are used in this course.

I'd welcome any suggestions for additions or other changes.

1 Microstates

A microstate is a quantum-mechanical state of the *entire system* being considered; in statistical mechanics we are often interested in systems that comprise many components (e.g. many particles). Each microstate has a well-defined energy, known from quantum mechanics.

1.1 Principle of equal equilibrium probability (PEEP)

An isolated system, whose energy is therefore constant, explores all the W microstates that have that energy, with equal probabilities $1/W$.

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[1] Sections 1, 2, 3, 7, 8 and 10 are mainly fundamental statistical mechanics, while Sections 4, 5, 6 and 9 contain mainly applications.

1.2 Density of microstates

The number of microstates (i.e.) whose energies lie between E and $E + dE$ is $g(E)\,dE$. For large systems $g(E)$ and W may, to a good approximation, be used interchangeably; in particular, $\ln g$ differs negligibly from $\ln W$.

2 Thermal Equilibrium, Temperature

2.1 Definition of Temperature

For a large system,

$$\frac{1}{kT} = \frac{d \ln g(E)}{dE} \,. \tag{2.1}$$

This quantity will be equalised when two large systems are able to exchange energy and reach equilibrium (i.e. thermal equilibrium).

2.2 Boltzmann distribution

Probability of a system (large or small) being in microstate i, where the system is able to exchange energy with a heat reservoir at temperature T, is

$$p_i = \frac{e^{-E_i/kT}}{Z} \,, \tag{2.2}$$

where E_i is the energy of microstate i, and Z is the partition function

$$Z = \sum_j e^{-E_j/kT} \,. \tag{2.3}$$

The partition function $Z(T)$ may be used to calculate many things conveniently. For example, the mean energy may be obtained from Z using the result

$$\bar{E} = \sum_i p_i E_i = -\frac{\partial Z}{\partial \beta} / Z = -\frac{\partial \ln Z}{\partial \beta} \,, \tag{2.4}$$

where $\beta = 1/kT$.

3 Entropy

3.1 Entropy of an isolated system

The qualitative idea of entropy is to measure how many microstates a system is exploring with significant probability. For a isolated system, or a system sufficiently large that its energy fluctuates very little, Boltzmann defined

$$S = k \ln W \,, \tag{3.1}$$

where W is the number of microstates that the system is exploring (with equal probability, from PEEP)[2].

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[2] Real systems have a unique ground state, so at very low temperatures W is effectively 1, so $S = 0$: this is the third law of thermodynamics.

3.2 Entropy of a general system

The more general expression for entropy is the Gibbs formula

$$S = -k \sum_i p_i \ln p_i\,, \tag{3.2}$$

where the system is exploring each microstate with probabilities p_i (not generally equal). For an isolated system in a steady state, $S = k \ln W$ is regained[3].

3.3 Entropy and Helmholtz free energy of a system at constant T

$$F = \bar{E} - TS = -kT \ln Z\,. \tag{3.3}$$

3.4 Meaning of heat, contact with thermodynamic entropy

Calculus shows that the change in the mean energy of a system is given by

$$d\bar{E} = d(\sum_i p_i E_i) = \underbrace{\sum_i E_i\, dp_i}_{dq_{\text{rev}}} + \underbrace{\sum_i p_i\, dE_i}_{dw_{\text{rev}}}\;. \tag{3.4}$$

For a reversible (i.e. slow) change, these terms may be identified as, respectively, the heat that enters the system dq_{rev} and the work done on the system dw_{rev} as indicated below the terms above[4]. Then $dS = dq_{\text{rev}}/T$, establishing contact with thermodynamic entropy.

4 Applications

4.1 Configurational entropy

Use $S = k \ln W$ directly, using permutation theory to evaluate W, the number of configurations, and then (for a system at constant volume and temperature) mimimise $F = \bar{E} - TS$. (The example studied was the concentration of vacancies in a crystal at temperature T.)

4.2 Mean energy of a simple harmonic oscillator

$$\bar{E} = \tfrac{1}{2}\hbar\omega + \frac{\hbar\omega}{e^{\hbar\omega/kT} - 1}\,, \tag{4.1}$$

the Planck oscillator formula, follows from applying the Boltzmann distribution. The heat capacity is then

$$C = d\bar{E}/dT = k\frac{x^2 e^x}{(e^x - 1)^2}\,, \tag{4.2}$$

where $x = \hbar\omega/kT$. At high T (specifically, $kT \gg \hbar\omega$), these expressions become simply kT and k respectively (an example of equipartition[5]).

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[3] And as the isolated system's steady state is approached, S as given by the Gibbs formula increases to a maximum: this is the second law of thermodynamics.

[4] This is the first law of thermodynamics. Strictly, dw_{rev} should be termed the work done *by varying the macroscopic constraints* – e.g. by changing the volume of a container of gas.

[5] The equipartition theorem is a general result, applicable when $kT \gg$ quantum energy spacing (i.e. in the classical limit), which states that each degree of freedom in the energy that is proportional to (displacement)^2 or (velocity)^2 acquires a mean value of $\frac{1}{2}kT$. In the oscillator there are two such terms: the kinetic energy and the potential energy, hence kT.

5 Vibrational Energy of a Solid

In a crystal of N vibrating atoms, dimensions $L \times L \times L$, each vibrational mode may be characterised by the 3 components of its wavevector $\mathbf{q} = (q_x, q_y, q_z)$, where each component[6] is a positive integer times π/L. (This important method of counting states in $\mathbf{q}$-space is also used in Sections 6, 8 and 9 of the course.) There are 3 vibrational modes for each $\mathbf{q}$.

5.1 Einstein model

In this rather crude model, each vibrational mode is taken to have the same angular frequency, ω_{E}, so the heat capacity is simply that of a single oscillator (Eq. 4.2) multiplied by $3N$, the number of modes. It is exponentially small at low T, a feature not observed in real solids.

5.2 Debye model

Here we take a more realistic dispersion relation, $\omega = cq$, where c is a constant (the speed of sound, in effect). The total heat capacity involves a sum over modes which may be evaluated by integrating over q (here, from 0 to $q_{\max}$, where $q_{\max}$ is chosen to encompass exactly $3N$ modes), noting that the volume of the positive octant of a spherical shell is $4\pi q^2 dq/8$, and making use of the number of $\mathbf{q}$-points per unit volume of $\mathbf{q}$-space (V/π^3), the number of modes per $\mathbf{q}$ (3), and the contribution of each mode:

$$C = \frac{3k^4T^3V}{2\pi^2\hbar^3c^3} \int\limits_0^{\hbar c q_{\max}/kT} \frac{x^4 e^x}{(e^x - 1)^2}\, dx\,, \tag{5.1}$$

where $V = L^3$ and $q_{\max} = (6\pi^2 N/V)^{1/3}$. This goes to $3Nk$ at high T and falls to zero proportional to T^3 at low T.

6 The Ideal Gas

6.1 Partition function of the ideal gas

$$Z = \frac{Z_1^N}{N!} = \frac{V^N}{N!}\left(\frac{mkT}{2\pi\hbar^2}\right)^{3N/2}, \tag{6.1}$$

where Z_1 is calculated using state counting in $\mathbf{q}$-space (see above). From Z, the free energy F is readily obtained using $F = -kT\ln Z$. (Here, as so often in this course, it's convenient to use Stirling's approximation $\ln N! \approx N\ln N - N$.)

6.2 Pressure and mean (translational) energy of the ideal gas

$$PV = NkT\,, \tag{6.2}$$

the ideal gas law, establishes the equivalence of T to the ideal gas temperature. Also

$$\bar{E} = \tfrac{3}{2}NkT\,. \tag{6.3}$$

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[6] See the guide "*Key Maths and Physics for Statistical Mechanics*" for details of the quantisation of waves in a box.

6.3 Maxwell-Boltzmann distribution of molecular speed, c

$$f(c) = \frac{1}{2\pi^2}\left(\frac{2\pi m}{kT}\right)^{3/2} c^2\, e^{-mc^2/2kT} \tag{6.4}$$

6.4 Heat capacity of a diatomic molecular gas like O_2

To the translational heat capacity $\frac{3}{2}Nk$ is added a further Nk from rotation ($kT \gg$ rotational energy spacing) and a much smaller contribution (at normal temperatures) from vibration ($kT <$ vibrational energy spacing).

7 Systems with Variable Numbers of Particles

7.1 Chemical potential

$$-\frac{\mu}{kT} = \left(\frac{\partial \ln g(E,N)}{\partial N}\right)_E . \tag{7.1}$$

This quantity will be equalised (along with T) when two large systems are able to exchange energy *and particles*.

The useful TdS equation is extended to

$$d\bar{E} = TdS - PdV + \mu dN . \tag{7.2}$$

7.2 Gibbs distribution

Probability of a system (large or small) being in microstate i, where the system is able to exchange energy and particles with a heat-and-particle reservoir at temperature T and chemical potential μ, is

$$p_i = \frac{e^{-(E_i-\mu N_i)/kT}}{\mathcal{Z}} , \tag{7.3}$$

where the grand partition function is

$$\mathcal{Z} = \sum_j e^{-(E_j-\mu N_j)/kT} . \tag{7.4}$$

The sum in $\mathcal{Z}$ is over all microstates, taking account of *all* possible values of N_j, the number of particles (unlike the ordinary Z in which only microstates with a particular value of N are summed over).

8 Identical Particles

8.1 Bose-Einstein distribution

The average number of identical bosons (spin quantum number s=0, 1, 2,...) in a single-particle state of energy ε is

$$f(\varepsilon) = \frac{1}{e^{(\varepsilon-\mu)/kT} - 1} . \tag{8.1}$$

At low temperatures, nearly all the particles condense into the single-particle state of lowest energy.

8.2 Fermi-Dirac distribution

For identical fermions ($s=\frac{1}{2}, \frac{3}{2}, ...$), the Pauli principle of quantum mechanics prohibits two or more fermions from occupying the same single-particle state (where we count the different spin orientations as distinct single-particle states). The average number of identical fermions in a single-particle state of energy ε is

$$f(\varepsilon) = \frac{1}{e^{(\varepsilon-\mu)/kT} + 1}\,. \tag{8.2}$$

At low temperatures, all single-particle states up to the Fermi energy ε_{F} (the chemical potential at $T = 0$) contain 1 fermion (i.e. are fully occupied), and higher states contain zero fermions.

8.3 Determination of chemical potential

In both the above distributions, μ must be chosen (at each T) so that $f(\varepsilon)$, summed over all single-particle states, equals N, the number of particles known to be in the system.

9 Black-Body Radiation

9.1 Energy density

Energy per unit volume in electromagnetic modes of a vacuum, excluding the T-independent zero-point energy, is

$$\varepsilon = \frac{\bar{E}}{V} = \frac{\pi^2 k^4}{15\hbar^3 c^3} T^4 = \int_0^\infty \varepsilon_\omega(\omega)\, d\omega\,, \tag{9.1}$$

where the spectral energy density (i.e. resolved into contributions from each ω) is given by

$$\varepsilon_\omega(\omega) = \frac{\hbar\omega^3}{\pi^2 c^3 \left(e^{\hbar\omega/kT} - 1\right)}\,. \tag{9.2}$$

(As usual, ω is related to wavelength by $\omega = 2\pi c/\lambda$.)

9.2 Energy flux

The electromagnetic energy flux impinging on (and, for a black body, emitted by) a solid surface per unit area per unit time is σT^4, where

$$\sigma = \frac{\pi^2 k^4}{60\hbar^3 c^2} \tag{9.3}$$

is known as the Stefan-Boltzmann constant.

10 Classical Statistical Mechanics

This non-examinable section of the course is a brief introduction to how statistical mechanics was originally (and, of course, not fully correctly) formulated before the theory of quantum mechanics existed.