

4211 Statistical Mechanics

Brian Cowan

Email b.cowan@rhul.ac.uk

Course web pages <http://personal.rhul.ac.uk/UHAP/027/PH4211/>

You will be redirected here from the MOODLE page

Statistical Mechanics

‘Ludwig Boltzmann, who spent much of his life studying statistical mechanics, died in 1906, by his own hand. Paul Ehrenfest, carrying on the work, died similarly in 1933. Now it is our turn to study statistical mechanics.

Perhaps it will be wise to approach the subject cautiously.’

David Goodstein— in *States of Matter*, 1975, Dover N.Y.



Statistical Mechanics



‘Statistical mechanics / thermodynamics, being what many consider to be one of the most intellectually difficult subjects of all, is noted for its prevalence of suicides and suicide attempts by a significant number of its founders’



!! Deep thinking – Depression !!





Statistical Mechanics



Robert Mayer: 1850 – jumped out of a 3rd-floor window

Ludwig Boltzmann: 1906 – hanged himself

Paul Ehrenfest: 1933 – shot his daughter and himself

Fritz Haber's family: 1915 – wife shot herself; 1947, both son and daughter shot themselves..**Otto.Sackur1914**

Gilbert Lewis: 1946 – took cyanide after not getting Nobel prize

Alan Turing: 1954 – bit into a cyanide-laced apple

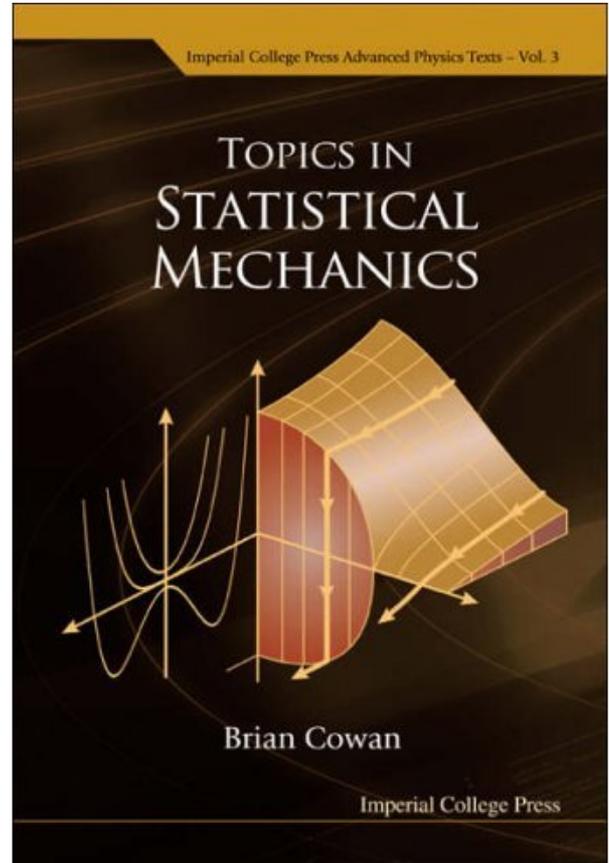
Percy Bridgman: 1961 – shot himself

Statistical Mechanics

This is a ‘paperless course’
See course web pages for:

- Course details – syllabus etc.
- Lecture timetable / calendar
- Lecture notes
- Problem sheets
- Other useful information
- Past exam papers

And FANTASTIC book!!!!!!



Course Outline

- Methodology of Statistical Mechanics
- Non-Ideal Gases
- Phase Transitions
- Fluctuations and Dynamics

Chapter 1

The Methodology of Statistical Mechanics

1.1 Terminology and Methodology

1.1.1 Approaches to the subject

Thermodynamics is the study of the relationship between *macroscopic* properties of systems, such as temperature, volume, pressure, magnetisation, compressibility etc. etc.

Statistical Mechanics is concerned with understanding how the various macroscopic properties arise as a consequence of the *microscopic* nature of the system. In essence it makes macroscopic deductions from microscopic models.

Albert Einstein.....

‘A theory is the more impressive the greater the simplicity of its premises is, the more different kinds of things it relates, and the more extended is its area of applicability.

Therefore the deep impression which classical thermodynamics made upon me; it is the only physical theory of universal content concerning which I am convinced that, within the framework of the applicability of its basic concepts, will never be overthrown.’

Autobiographical Notes, Albert Einstein: Philosopher-Scientist, Ed. P. A. Schilpp, Open Court Publishing Co. 1949

Lev Landau.....

‘Statistical physics and thermodynamics together form a unit.

All the concepts and quantities of thermodynamics follow most naturally, simply and rigorously from the concepts of statistical physics.

Although the general statements of thermodynamics can be formulated non-statistically, their application to specific cases always requires the use of statistical physics.’

In the Preface to *Statistical Physics*, vol 5 of Landau and Lifshitz Course of Theoretical Physics.

Arnold Sommerfeld (not actually relevant, but....)

Sommerfeld was asked why he had never written a book on thermodynamics – having written books on most other areas of physics. He replied:

“Thermodynamics is a funny subject. The first time you go through it, you don't understand it at all. The second time you go through it, you think you understand it, except for one or two small points. The third time you go through it, you know you don't understand it, but by that time you are so used to it, it doesn't bother you anymore.”

However later, in 1951, writing a book on thermodynamics and statistical mechanics, he was killed following a traffic accident. The book was published posthumously the following year.

Relationship between Statistical Mechanics and Thermodynamics

PARADOX I

Landau: disciplines are ‘**similar**’ – **reductionism** –
Thermodynamics *explained* by Statistical Mechanics

Einstein: disciplines are ‘**opposites**’ – the domain of
Thermodynamics is independent of the microscopics

Resolution – concept of **emergence** – Macroscopic behaviour is
consistent with microscopic description, but *robust* against
microscopic details.

PARADOX II

Landau’s and Einstein’s actual work!!!!!!!!!!

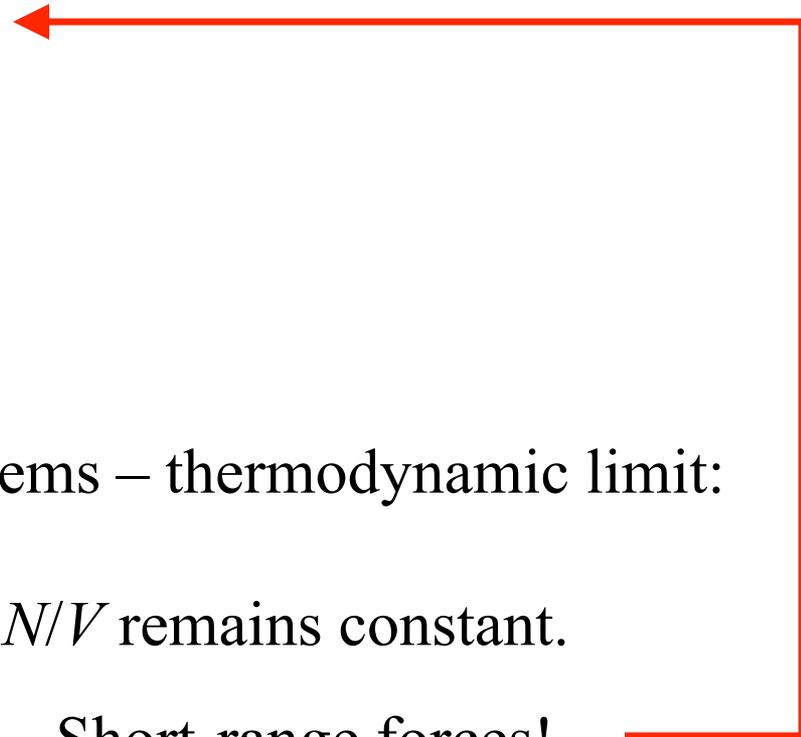
1.1.2 Description of states

Macrostate

Microstate

1.1.3 Extensivity and the Thermodynamic Limit

- Extensive variables
- Intensive variables



Stat. Mech. deals with large systems – thermodynamic limit:

$N \rightarrow \infty$, $V \rightarrow \infty$, while N/V remains constant.

Surface effects can be neglected – Short-range forces!

1.2 The Fundamental Principles

1.2.1 The laws of thermodynamics

- Zeroth Law
- First Law
- Second Law
- Third Law

Zeroth Law

If system A is in equilibrium with system B and system A is in equilibrium with system C then system B is in equilibrium with system C .

- Equilibrium of 2 bodies: No change when put together
- The existence of equilibrium states
- The existence of temperature: subtle – but essentially simple arguments. See Pippard (or Adkins).

First Law

The internal energy of a body can change by the flow of heat or by doing work.

$$\Delta E = \Delta Q + \Delta W$$

Beware: different sign convention for ΔW in older books.

Physics of the First Law is obvious to us – but it is important in the historical context: *heat is a form of energy*.

Second Law

Clausius: Heat flows from hot to cold.

Kelvin: It is not possible to convert *all* heat energy to work.

Carathéodory: In the neighbourhood of any equilibrium state of a thermally isolated system there are states which are inaccessible. (Discussion in Adkins)

Callen: There is an extensive quantity, which we call entropy, which never decreases in a physical process.

Third Law

Nernst, Simon and others

The entropy of a body tends to zero as the temperature tends to absolute zero.

1.2.2 Probabilistic interpretation of the First Law

macrostate

microstate

$$E = \sum_j P_j E_j$$

$$dE = \sum_j P_j dE_j + \sum_j E_j dP_j$$

$$\sum_j P_j dE_j = dW$$

Shifting energy levels

$$\sum_j E_j dP_j = dQ$$

Changing populations of states

Work

Heat

1.2.3 Microscopic basis for entropy

Postulate – All microstates of an *isolated system* are equally likely. Isolated system specified by E, V, N .

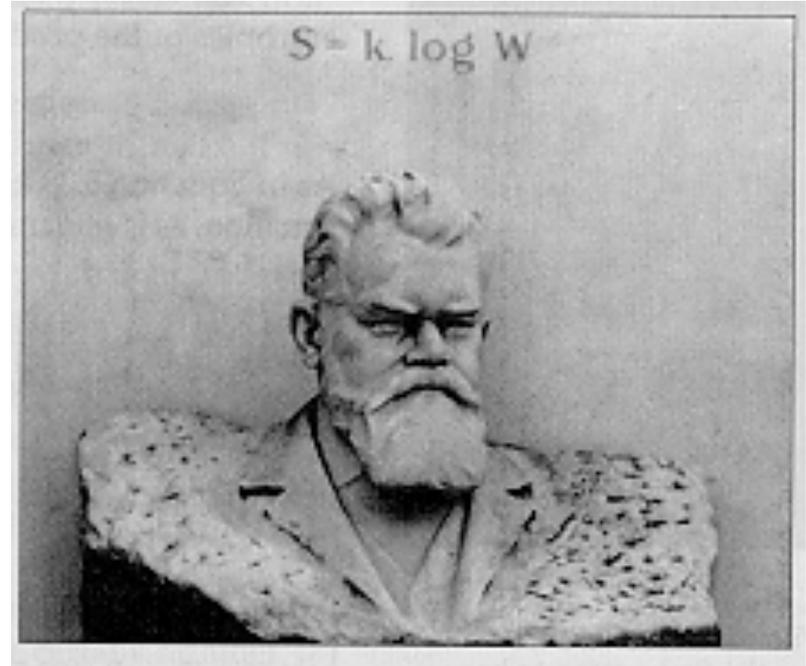
$\Omega(E, V, N)$ is number of microstates in macrostate (E, V, N)

$$P(E, V, N) \propto \Omega(E, V, N)$$

Ω is multiplicative, so $\ln \Omega$ is additive – *extensive* variable

So define *entropy* S :

$$S(E, V, N) = k \ln \Omega(E, V, N)$$

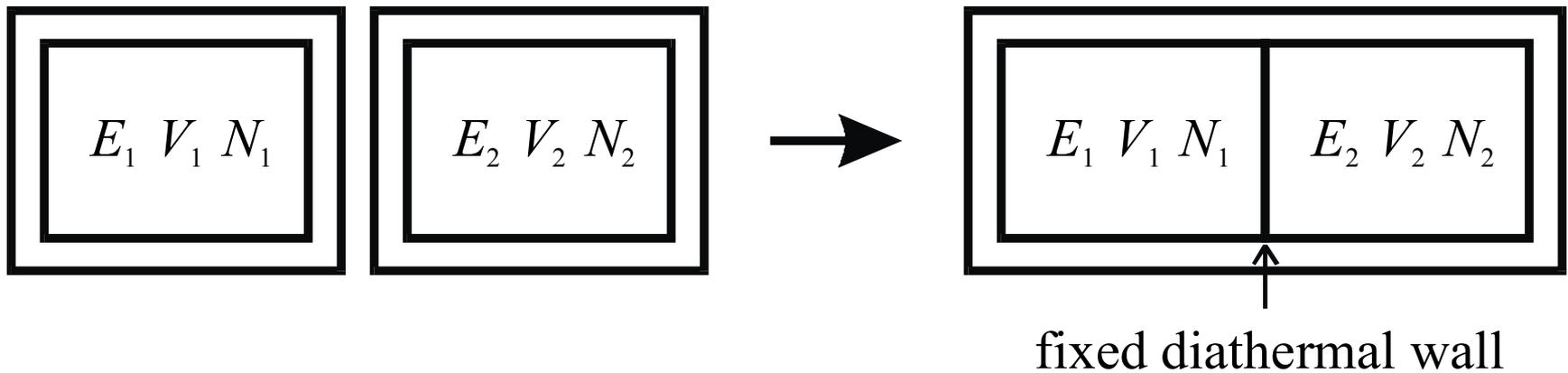


Ludwig Boltzmann
1844 - 1902

1.3 Interactions – The conditions for Equilibrium

When systems interact their states will often change, the composite system evolving to a *state of equilibrium*. We shall investigate what determines the final state. We will see that quantities such as temperature emerge in the description of these equilibrium states.

1.3.1 Thermal interaction – Temperature



1.3.1 Thermal interaction – Temperature

E_1 and E_2 can vary subject to $E_1 + E_2 = \text{const} = E_0$.

1.3.1 Thermal interaction – Temperature

E_1 and E_2 can vary subject to $E_1 + E_2 = \text{const} = E_0$.

$$\Omega = \Omega_1(E_1)\Omega_2(E_2)$$

$$\Omega = \Omega_1(E)\Omega_2(E_0 - E)$$

Maximise Ω by varying E .

$$\frac{d\Omega}{dE} = \frac{d\Omega_1}{dE}\Omega_2 - \Omega_1\frac{d\Omega_2}{dE} = 0$$

$$\frac{1}{\Omega_1}\frac{d\Omega_1}{dE} = \frac{1}{\Omega_2}\frac{d\Omega_2}{dE}$$

$$= 1/T$$

log occurs
naturally

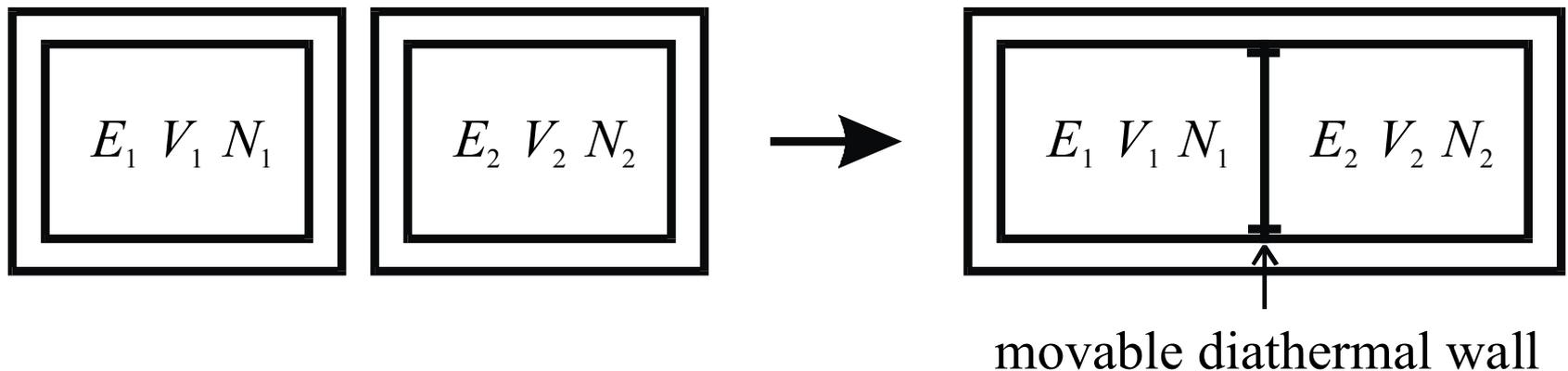
$$\frac{d\ln\Omega_1}{dE} = \frac{d\ln\Omega_2}{dE}$$

or

$$\frac{dS_1}{dE} = \frac{dS_2}{dE}$$

condition for
equilibrium

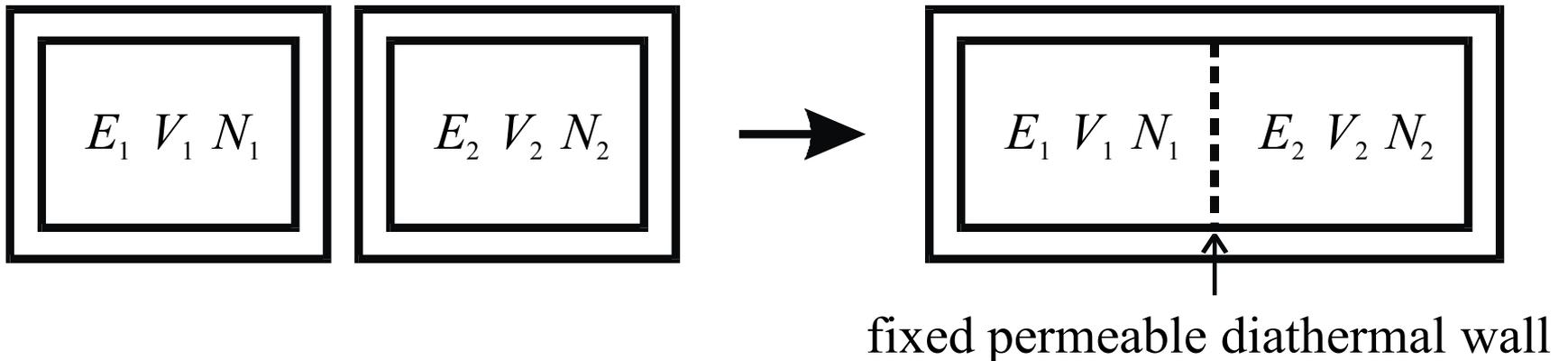
1.3.2 Volume change – Pressure and thermal interaction



- Callen paradox – if wall is *not* diathermal.

1.3.3 Particle interchange – chemical potential.

and thermal interaction



1.3.2 /1.3.3 Energy, volume and particle interchange

E_1 and E_2 can vary subject to $E_1 + E_2 = \text{const} = E_0$.

V_1 and V_2 can vary subject to $V_1 + V_2 = \text{const} = V_0$.

N_1 and N_2 can vary subject to $N_1 + N_2 = \text{const} = N_0$.

$$\begin{aligned}\Omega &= \Omega_1(E_1, V_1, N_1)\Omega_2(E_2, V_2, N_2) \\ &= \Omega_1(E, V, N)\Omega_2(E_0 - E, V_0 - V, N_0 - N).\end{aligned}$$

We maximize Ω by varying E, V, N : (partial derivatives)

$$\frac{\partial \Omega}{\partial E} = \frac{\partial \Omega_1}{\partial E} \Omega_2 - \Omega_1 \frac{\partial \Omega_2}{\partial E} = 0 \implies \frac{1}{\Omega_1} \frac{\partial \Omega_1}{\partial E} = \frac{1}{\Omega_2} \frac{\partial \Omega_2}{\partial E}$$

$$\frac{\partial \Omega}{\partial V} = \frac{\partial \Omega_1}{\partial V} \Omega_2 - \Omega_1 \frac{\partial \Omega_2}{\partial V} = 0 \implies \frac{1}{\Omega_1} \frac{\partial \Omega_1}{\partial V} = \frac{1}{\Omega_2} \frac{\partial \Omega_2}{\partial V}$$

$$\frac{\partial \Omega}{\partial N} = \frac{\partial \Omega_1}{\partial N} \Omega_2 - \Omega_1 \frac{\partial \Omega_2}{\partial N} = 0 \implies \frac{1}{\Omega_1} \frac{\partial \Omega_1}{\partial N} = \frac{1}{\Omega_2} \frac{\partial \Omega_2}{\partial N}$$

The log occurs naturally.

These are the conditions for equilibrium

$$\frac{\partial \ln \Omega_1}{\partial E} = \frac{\partial \ln \Omega_2}{\partial E} \quad \text{or} \quad \frac{\partial S_1}{\partial E} = \frac{\partial S_2}{\partial E}$$

$$\frac{\partial \ln \Omega_1}{\partial V} = \frac{\partial \ln \Omega_2}{\partial V} \quad \text{or} \quad \frac{\partial S_1}{\partial V} = \frac{\partial S_2}{\partial V}$$

$$\frac{\partial \ln \Omega_1}{\partial N} = \frac{\partial \ln \Omega_2}{\partial N} \quad \text{or} \quad \frac{\partial S_1}{\partial N} = \frac{\partial S_2}{\partial N}$$

Conditions for equilibrium:

$\partial S/\partial E$ equalized

$\partial S/\partial V$ equalized

$\partial S/\partial N$ equalized

What do these mean?

From the (extended) First Law

$$dE = TdS - pdV + \mu dN$$

we get

$$dS = \frac{1}{T}dE + \frac{p}{T}dV - \frac{\mu}{T}dN$$

So we identify the derivatives

$$\frac{\partial S}{\partial E} = \frac{1}{T}, \quad \frac{\partial S}{\partial V} = \frac{p}{T}, \quad \frac{\partial S}{\partial N} = -\frac{\mu}{T}.$$

So temperature is equalized when energy flows

Pressure also is equalized when “volume” flows

Chemical potential also is equalized when particles flow.

Callen paradox

1.3.4 Thermal interaction with the rest of the world – The Boltzmann factor

The Canonical distribution function

Isolated system : all microstates equally likely.

What about non-isolated system?

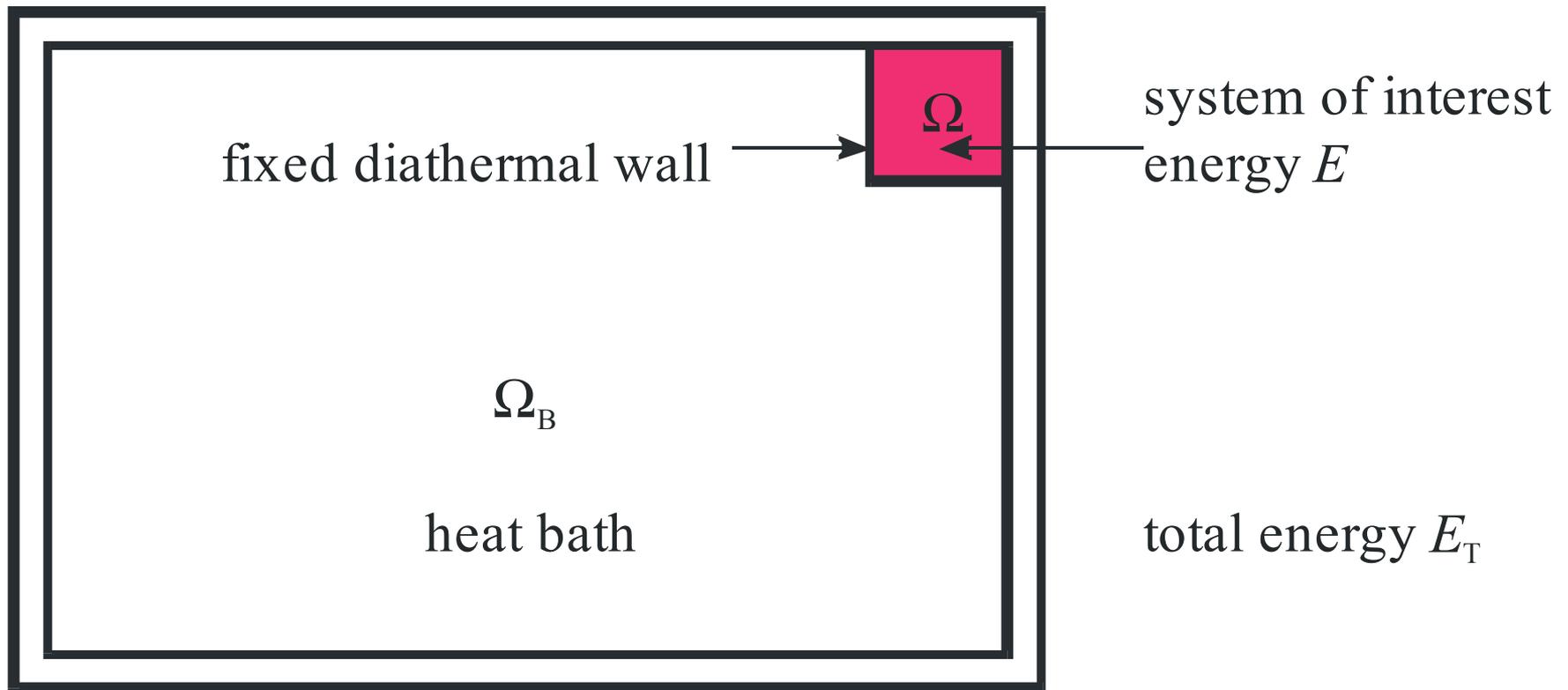
What is the probability that a non-isolated system is found in a microstate of energy E ?

Non-isolated (here) means bounded by a *fixed, diathermal* wall.

“Extend” our Fundamental Postulate

1.3.4 Thermal interaction with the rest of the world – The Boltzmann factor

The Canonical Distribution Function



1.3.4 Thermal interaction with the rest of the world — The Boltzmann factor **Canonical distribution function**

$$P(E) \propto \Omega_B(E_T - E)\Omega(E)$$

$\uparrow = 1$ (single microstate)

i.e.

$$P(E) \propto \Omega_B(E_T - E)$$

Work in terms of entropy $S = k \ln \Omega$ — *entropy of bath*.

$$P(E) \propto e^{S(E_T - E)/k}.$$

Since $E \ll E_T$, we can do a Taylor expansion:

Taylor expansion

$$S(E_T - E) = S(E_T) - E \frac{\partial S}{\partial E} + \dots$$

But $\frac{\partial S}{\partial E} = \frac{1}{T}$ (temperature of bath).

So $S(E_T - E) = S(E_T) - \frac{E}{T} + \dots$

If we can ignore higher order terms

$$P(E) \propto e^{S(E_T)/k} e^{-E/kT} .$$

$\uparrow =$ constant.

$$P(E) \propto e^{-E/kT} .$$

1.3.4 Thermal interaction with the rest of the world – The Boltzmann factor

The Canonical Distribution Function

$$P(E) \propto e^{-E/kT}$$

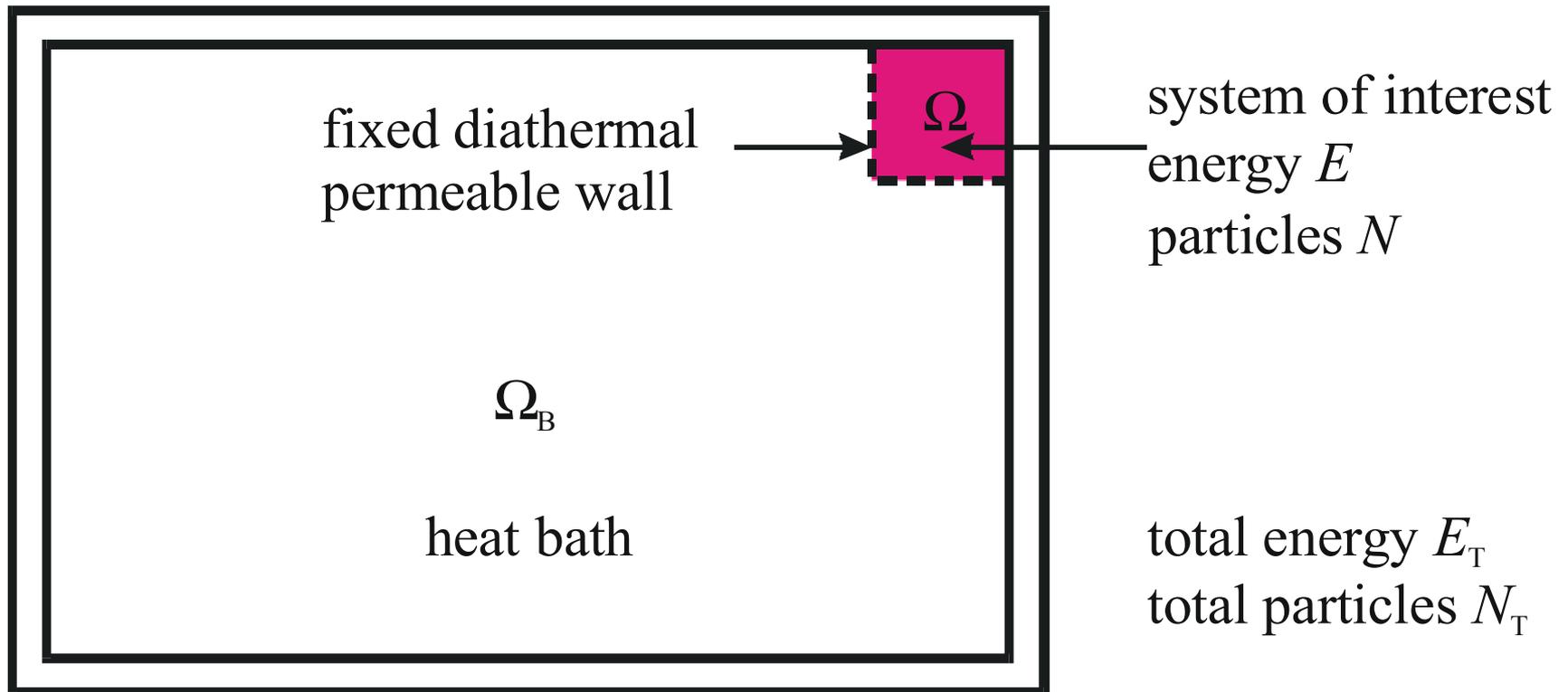
The Boltzmann factor is a key result. Richard Feynman says:

“This fundamental law is the summit of statistical mechanics, and the entire subject is either a slide-down from the summit, as the principle is applied to various cases, or the climb-up to where the fundamental law is derived and the concepts of thermal equilibrium and temperature clarified”.

R. P. Feynman, *Statistical Mechanics*, Benjamin 1972.

1.3.5 Particle and energy exchange with the rest of the world – the Gibbs factor

The Grand Canonical Distribution Function



1.4 Thermodynamic averages

1.4.1 The partition function

$$P(E) \propto e^{-E/kT}$$

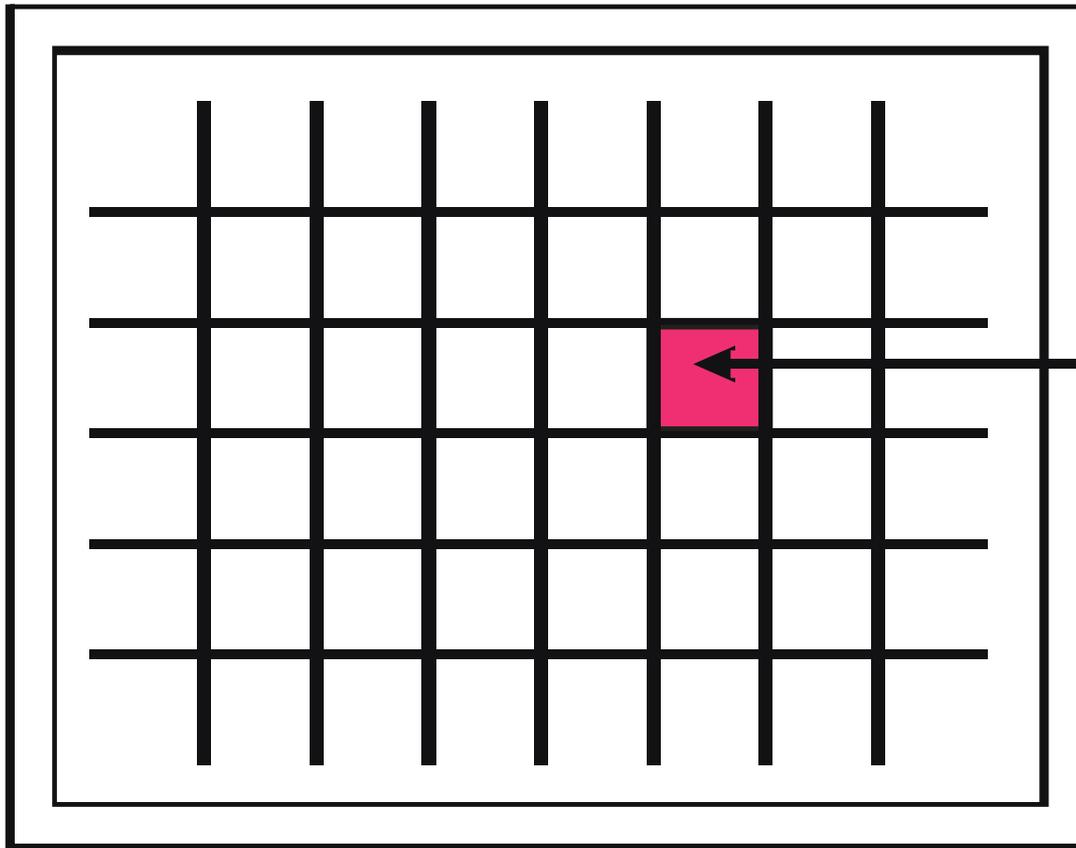
$$P(E) = \frac{e^{-E/kT}}{Z}$$

$$Z = \sum_j e^{-E_j/kT}$$

Z is the “partition” function – **amazingly important!**

1.4.2 Generalised expression for Entropy

collection of M identical systems



system of interest

$$\begin{aligned} S &= -k \sum_j P_j \ln P_j \\ &= -k \langle \ln P_j \rangle. \end{aligned}$$

Take M identical systems (in same *macrostate*).

There are n_j of these in the j th microstate.

The no. of micro states of the composite system =
the no. of ways of re-arranging the subsystems:

$$\Omega = \frac{M!}{n_1!n_2!n_3!\dots}$$

so the total entropy is

$$S_{\text{tot}} = k \ln \left(\frac{M!}{n_1!n_2!n_3!\dots} \right).$$

Use *Stirling's approximation*: $\ln n! \approx n \ln n - n$, giving

$$S_{\text{tot}} = k \left(M \ln M - M - \sum_j n_j \ln n_j + \cancel{\sum_j n_j} \right).$$

Now put the first M as $\sum_j n_j$, then

$$S_{\text{tot}} = k \left(\sum_j n_j \ln M - \sum_j n_j \ln n_j \right) = -k \sum_j n_j \ln \left(\frac{n_j}{M} \right).$$

Mean entropy of our particular system is $1/M$ of this:

$$S = -k \sum_j \frac{n_j}{M} \ln \left(\frac{n_j}{M} \right) = -k \sum_j P_j \ln P_j$$

since $P_j = n_j/M$. $= -k \left\langle P_j \right\rangle$ Gibbs entropy

1.4.3 Free Energy

$$P_j(N, V, T) = \frac{e^{-E_j(N, V)/kT}}{Z(N, V, T)}, \quad Z(N, V, T) = \sum_j e^{-E_j(N, V)/kT}$$

$$\ln P_j = - \left(\frac{E_j}{kT} + \ln Z \right)$$

$$S = k \left\langle \frac{E_j}{kT} + \ln Z \right\rangle$$

$$S = \frac{E}{T} + k \ln Z$$

$$E - TS = -kT \ln Z$$

$$F = E - TS$$

$$F = -kT \ln Z$$

1.4.4 Thermodynamic Variables

A host of thermodynamic variables can be obtained from the partition function. This is seen from the differential of the free energy.

$$dE = TdS - pdV + \mu dN$$

but $F = E - TS$

so that $dF = -SdT - pdV + \mu dN$

Then we can identify the partial derivatives:

1.4.4 Thermodynamic Variables

$$dF = -SdT - pdV + \mu dN$$

so that
$$S = -\left.\frac{\partial F}{\partial T}\right|_{V,N} = kT \left.\frac{\partial \ln Z}{\partial T}\right|_{V,N} + k \ln Z$$

$$p = -\left.\frac{\partial F}{\partial V}\right|_{T,N} = kT \left.\frac{\partial \ln Z}{\partial V}\right|_{T,N}$$

$$\mu = \left.\frac{\partial F}{\partial N}\right|_{T,V} = -kT \left.\frac{\partial \ln Z}{\partial N}\right|_{T,V}$$

and then
$$E = F + TS = kT^2 \left.\frac{\partial \ln Z}{\partial T}\right|_{V,N}$$

★ So all follows from differentiating Z .