1.6 Classical Statistical Mechanics

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Classical Statistical Mechanics

• Classical Mechanics is best formulated in terms of position \( (q) \) and momenta \( (p) \) coordinates (inc. generalized coordinates).

• So we would say a state is specified when we know all the position and momenta coordinates.

• The \( p - q \) space is called phase space.

• So in classical mechanics a state is a point in phase space.

• Difficulty in counting such states since \( p \) and \( q \) vary continuously; there would be an infinite number of states in any region of phase space.

• In Statistical Mechanics it is expedient to erect a grid in phase space with cells \( \Delta q_x \Delta q_y \Delta q_z \Delta p_x \Delta p_y \Delta p_z \).
In classical statistical mechanics a state corresponds to a cell in phase space.

- I.e. a system is in a given (micro) state if it is in a specified cell in phase space.

- What should be the size of the cells?

- Dimension of $p \times q$ is action (like in Planck’s constant $\hbar$).
• We argue that the precise size of the cells should not be important.

• But we note that Quantum Mechanics (Uncertainly principle) tells us we cannot discern a state to finer than a $\Delta p \Delta q$ cell smaller than Planck’s constant.

Our Philosophy
• We shall write the size of a $\Delta p \Delta q$ cell as $h$. At this stage its size will be undetermined. Later, by comparing results with those calculated by quantum statistical mechanics, we will identify this $h$ as Planck’s constant.

Connection between classical/quantum statistical mechanics
• The general rule is that sums over states in the quantum case correspond to integrals over phase space in the classical case.

$$\sum_{\text{single particle states}} \rightarrow \frac{1}{h^3} \int d^3p \ d^3q$$

Note the appearance of the $h$ factors ensures dimensionality.
1.6.2 Boltzmann and Gibbs Phase Spaces

(Transatlantic communication in latter half of 19th Century)

**Boltzmann:**

Phase space has 6 dimensions: 3 position coordinates \( q_x, q_y, q_z \).

3 momentum coordinates \( p_x, p_y, p_z \).

State of a system comprising \( N \) particles represented by \( N \) points in this 6 dimensional phase space.

**Gibbs:**

Phase space has \( 6N \) dimensions: 3 \( q \)’s and 3 \( p \)’s for each particle.

State of this system represented by 1 point in this \( 6N \) dimensional space.
1.6.3 The Fundamental Postulate in the Classical Case

The classical version of the Fundamental Postulate states that for an isolated system all available regions of phase space on the constant energy hypersurface are equally likely.
1.6.4 The classical partition function

The classical analogue of the quantum partition function is given by

\[ Z = \frac{1}{h^{3N}} \int e^{-H(p_i, q_i)/kT} \, d^{3N}p \, d^{3N}q \]

The function \( H(p_i, q_i) \) is the energy of the system expressed as a function of the position and momentum coordinates \( \{q_i\} \) and \( \{p_i\} \). This is the *Hamiltonian*. 
1.6.5 The equipartition theorem

Energy of $i^{th}$ degree of freedom (from $p_i$)

$$\langle E_i \rangle = \frac{1}{Z} \int E_i e^{-E(q_1...q_i...q_N, p_1...p_i...p_N)/kT} d^3q d^3N p$$

\[\text{--- no } p_i \text{ ---}\]

\[\downarrow \quad \downarrow\]

$$\langle E_i \rangle = \frac{\int E_i e^{-E_i/kT} dp_i \int e^{-E(q_1...q_i...q_N, p_1.....p_N)/kT} d^3N q d^{3N-1} p}{\int e^{-E_i/kT} dp_i \int [\text{same integral as above - no } p_i]}$$

$$\langle E_i \rangle = \frac{\int E_i e^{-E_i/kT} dp_i}{\int e^{-E_i/kT} dp_i}$$

Use the beta trick: $\beta = 1/kT$....
The beta trick

Quantities like

\[ E e^{-E/kT} \]

we might wish to sum or integrate.

Put \( 1/kT \) to \( \beta \), so we have

\[ E e^{-\beta E} . \]

We can "bring down" the \( E \) by differentiating \( e^{-\beta E} \) with respect to \( \beta \):

\[ E e^{-\beta E} = - \frac{\partial}{\partial \beta} e^{-\beta E} . \]

This is the beta trick.
The beta trick gives

\[
\langle E_i \rangle = \frac{ \int E_i e^{-\beta E_i} \, dp_i }{ \int e^{-\beta E_i} \, dp_i } = - \frac{ \int \frac{\partial}{\partial \beta} e^{-\beta E_i} \, dp_i }{ \int e^{-\beta E_i} \, dp_i } .
\]

Interchange derivative and integral

\[
\langle E_i \rangle = - \frac{ \frac{\partial}{\partial \beta} \int e^{-\beta E_i} \, dp_i }{ \int e^{-\beta E_i} \, dp_i } .
\]

This is the derivative of the logarithm

\[
\langle E_i \rangle = - \frac{\partial}{\partial \beta} \ln \left[ \int e^{-\beta E_i} \, dp_i \right] .
\]

---

Note this
Next trick — you don’t need to do the integral; just change variables:

Let’s just put \( E_i = b p_i^2 \) and substitute \( \beta p_i^2 = y^2 \), so that

\[
\int e^{-\beta E_i} dp_i = \beta^{-1/2} \int e^{-by^2} dy .
\]

The logarithm of this is

\[
\ln \left[ \int e^{-\beta E_i} dp_i \right] = -\frac{1}{2} \ln \beta + \ln \left[ \int e^{-by^2} dy \right] .
\]

We have to differentiate with respect to \( \beta \) — so the integral drops out:

\[
\frac{\partial}{\partial \beta} \ln \left[ \int e^{-\beta E_i} dp_i \right] = - \frac{1}{2\beta} .
\]
We just found
\[ \frac{\partial}{\partial \beta} \ln \left[ \int e^{-\beta E_i} \, dp_i \right] = - \frac{1}{2\beta}. \]

And since we require
\[ \langle E_i \rangle = - \frac{\partial}{\partial \beta} \ln \left[ \int e^{-\beta E_i} \, dp_i \right] \]

Our result is that
\[ \langle E_i \rangle = \frac{1}{2\beta}. \]

So finally change back to \( kT = 1/\beta \), giving
\[ \langle E_i \rangle = \frac{kT}{2}. \]

(If \( E_i \propto p_i^n \) or \( q_i^n \) then corresponding \( \langle E_i \rangle = kT/n \) — even \( n \).)
Equipartition theorem:

For a classical (non-quantum) system, each degree of freedom with a quadratic dependence on coordinate or momentum gives a contribution to the internal energy of $kT/2$. 
1.6.6 Consequences of equipartition

- Each “quadratic” degree of freedom gives internal energy $kT/2$

Differentiate $E$ with respect to $T$ to obtain $C_V$:

- Lattice vibrations (both $p$ and $q$ contributions): $C_V = 3R$ per mol

- Gas of particles (only $p$ contribution): $C_V = \frac{3}{2}R$ per mol

($R$ is the gas constant $R = N_Ak$). Constant heat capacity!!

Equipartition breaks down when quantum effects become important – at low temperatures.
Liouville’s Theorem and Boltzmann’s H theorem

Can we understand the law of entropy increase from microscopic first principles?
1.6.7 Liouville’s theorem

Entropy – classical analogue of

\[ S = -k \sum_j P_j \ln P_j = -k \langle \ln P \rangle \]

is

\[ S = -k \int \rho \ln \rho \, d^n p \, d^n q = -k \langle \ln \rho \rangle \]

where \( \rho(p_i, q_i, t) = \) density of points in phase space.

Evolution of \( S \) (or \( \rho \)) with time? Should be consistent with Second Law.

But… Liouville’s theorem →

\[ \frac{d\rho}{dt} = 0 \]

- \( S \) appears to remain constant !!!!!!!!!!
1.6.8 Boltzmann’s $H$ theorem

Evolution of a region of phase space
1.6.8 Boltzmann’s $H$ theorem

Evolution of a region of phase space

Apparent reduction in density in phase space
Chapter 2
Practical Calculations with Ideal Systems

2.2 Identical Particles
2.2.1 Indistinguishability

If we had an assembly of $N$ identical but *distinguishable* particles the resultant partition function would be the product of the (same) partition functions of a single particle, $z$

$$Z = z^N.$$ 

The key question is that of *indistinguishability* of the atoms or molecules of a many-body system. When two identical molecules are interchanged the system is still in the same microstate, so the distinguishable particle result *overcounts* the states in this case.
Now the number of ways of redistributing \( N \) particles when there are \( n_1 \) particles in the first state, \( n_2 \) particles in the second state etc. is

\[
\frac{N!}{n_1! n_2! n_3! \ldots}
\]

so that for a given distribution \( \{n_i\} \) the partition function for identical indistinguishable particles is

\[
Z = \frac{n_1! n_2! n_3! \ldots}{N!} z^N.
\]
2.2.2 Classical approximation

In the classical case we have then

$$Z = \frac{1}{N!} z^N.$$  

The Helmholtz free energy

$$F = -kT \ln Z$$

is thus

$$F = -NkT \ln z + kT \ln N!.$$  

This is $N$ times the Helmholtz free energy for a single particle plus an extra term depending on $T$ and $N$. So the second term can be ignored so long as we differentiate with respect to something other than $T$ or $N$. Thus when differentiating with respect to volume to find the pressure, the result is $N$ times that for a single particle.
2.3 Ideal Classical Gas

2.3.2 Classical approach

The classical partition function is given by the integral

\[ z = \frac{1}{h^3} \int e^{-\epsilon/kT} d^3p \ d^3q \]

where for the ideal gas \( \epsilon = \frac{p^2}{2m} \). Thus the \( q \) integrals are trivial, giving a factor \( V \), and we have

\[ z = \frac{V}{h^3} \left[ \int_{-\infty}^{\infty} e^{-p^2/2mkT} \ dp \right]^3. \]

The integral is transformed to a pure number by changing variables: \( p = x\sqrt{2mkT} \) so that

\[ z = \frac{V}{h^3} (2mkT)^{3/2} \left[ \int_{-\infty}^{\infty} e^{-x^2} \ dx \right]^3. \]
As in the quantum calculation, the physics is all outside the integral and the integral is just a pure number. The value of the integral is $\sqrt{\pi}$ so that

$$z = \left( \frac{2\pi mkT}{h^2} \right)^{3/2} V$$

just as in the “quantum” calculation. This justifies the use of $h$ in the normalization factor for the classical state element of phase space.

Write

$$z = \frac{V}{\Lambda^3}, \quad \text{where} \quad \Lambda = \frac{h}{(2\pi mkT)^{3/2}}.$$

Here $\Lambda$ is known as the **thermal de Broglie wavelength**. It has a very important meaning.
2.3.3 Thermodynamic properties

We start from the Helmholtz free energy:

\[
F = -kT \ln Z = NkT \ln \left[ \left( \frac{2\pi mkT}{h^2} \right)^{3/2} \frac{Ve}{N} \right],
\]

giving

\[
p = kT \left. \frac{\partial \ln Z}{\partial V} \right|_{T,N} = NkT \left. \frac{\partial \ln z}{\partial V} \right|_{T} = \frac{NkT}{V}.
\]

This is the ideal gas equation, and from this we identify \( k \) as Boltzmann’s constant.

The internal energy is

\[
E = kT^2 \left. \frac{\partial \ln Z}{\partial T} \right|_{V,N} = NkT^2 \frac{d \ln T^{3/2}}{dT} = \frac{3}{2} NkT.
\]
This is the result we obtained previously from equipartition. This gives another important property of an ideal gas: the internal energy depends *only* on temperature (not pressure or density). This is known as Joule’s law. From the energy expression we obtain the thermal capacity

\[ C_V = \left. \frac{\partial E}{\partial T} \right|_{V,N} = \frac{3}{2} Nk. \]

This is a constant, independent of temperature, in violation of the Third Law. This is because of the classical approximation – ignoring multiple state occupancy etc. We also find the entropy and chemical potential:

\[
S = Nk \ln \left( \left( \frac{2\pi mkT}{\hbar^2} \right)^{3/2} \frac{kTe^{5/2}}{p} \right),
\]

\[
\mu = -kT \ln \left( \left( \frac{2\pi mkT}{\hbar^2} \right)^{3/2} \frac{kT}{p} \right).
\]
Sackur-Tetrode equation

\[ S = Nk \ln \left[ \left( \frac{2\pi mkT}{\hbar^2} \right)^{3/2} \frac{kTe^{5/2}}{p} \right] \]

\[ \Rightarrow \]

\[ S = \frac{5}{2} Nk \ln T - Nk \ln p + Nks_0 \]

- Latter equation can be derived by thermodynamics alone.
- Constant \( s_0 \) known as the Sakur-Tetrode constant

Naïve interpretation of this equation is wrong.
2.3.4 The $1/N!$ term in the partition function

The Gibbs paradox
Gibbs didn’t know about indistinguishable particles. So he wrote

$$Z = z^N.$$ 

We found

$$z = \left( \frac{2\pi mkT}{h^2} \right)^{3/2} V.$$ 

So (according to Gibbs)

$$F = -kT \ln Z = -NkT \ln z = -NkT \ln \left[ \left( \frac{2\pi mkT}{h^2} \right)^{3/2} V \right].$$

The right hand expression is NOT extensive.
The square bracket must be intensive - so you must divide $V$ by a dimensionless extensive quantity — like $N$. Gibbs chose $N$ and so he wrote

$$
F = - NkT \ln \left[ \left( \frac{2\pi mkT}{h^2} \right)^{3/2} \frac{V}{N} \right].
$$

We had a divisor of $N!$ in the partition function. Since by Stirling’s approximation, $\ln N! = N \ln(N/e)$, we found

$$
F = - NkT \ln \left[ \left( \frac{2\pi mkT}{h^2} \right)^{3/2} \frac{Ve}{N} \right].
$$