

Thermostatistique 2023-24 (LU3PY403)

correction des travaux dirigés

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TD1

HAMILTON'S EQ. / TD1 (Goldstein sec.)

Newton's law $m\ddot{\vec{r}} = \vec{F} = -\vec{\nabla}U$ is simple like this only in Cartesian coords! Often we like other coords due to symm. of U . Alternative law of motion is $\dot{x} = \partial H/\partial p_x$, $\dot{p} = -\partial H/\partial x$ $H = \text{energy}$. In Cartesian coord it is trivially equiv:

$$H = \frac{m\dot{\vec{r}}^2}{2} + U, \quad \frac{\partial H}{\partial p_x} = \frac{\vec{p}^2}{2m} + U, \quad \frac{\partial H}{\partial p_x} = p_x/m = \dot{x}, \quad -\frac{\partial H}{\partial x} = -\frac{\partial U}{\partial x} = F_x \\ = \dot{p}_x$$

But it's eq work in any coord system (as long as ch. of inv. is inviolate)

harm. osc. 2D:

$$m\ddot{x} = -kx \quad \omega = \sqrt{\frac{k}{m}} \quad H = \frac{p_x^2}{2m} + \frac{1}{2}kx^2 = \frac{p_x^2}{2m} + \frac{1}{2}m\omega^2 x^2$$

$$\ddot{x} = -m\omega^2 x$$

$$\left\{ \begin{array}{l} \dot{x} = \partial H / \partial p_x = p_x/m \\ \dot{p}_x = -\frac{\partial H}{\partial x} = -m\omega^2 x = m\ddot{x} \end{array} \right.$$

(Kepler) central force in 2D:

$$m\ddot{\vec{r}} = \vec{p} = \vec{F} = -\frac{\partial U}{\partial \vec{r}} = -k \frac{\vec{r}}{r^3} \quad U = -\frac{k}{r}$$

$$\left\{ \begin{array}{l} m\ddot{x} = F_x = -kx/r^3 \\ m\ddot{y} = F_y = -ky/r^3 \end{array} \right.$$

→ polar coords: $x = r \cos \theta$, $y = r \sin \theta$, $m\ddot{x} = ?$, $m\ddot{y} = ?$

$$\dot{x} = \dot{r} \cos \theta + r \sin \theta \dot{\theta}, \quad \dot{y} = \dot{r} \sin \theta + r \cos \theta \dot{\theta}$$

$$\ddot{x} = \dots \quad \ddot{y} = \dots$$

$$\rightarrow \left\{ \begin{array}{l} m\ddot{r} = -\frac{k}{r^2} + \frac{l^2}{mr^3} \\ \dot{l} = 0 \end{array} \right. \quad \begin{array}{l} \text{not Newton-line! "centrifugal force"} \\ (l = mr^2\dot{\theta}) \end{array} \quad \begin{array}{l} \text{"unreal" line Pauli!} \\ \rightarrow \text{numerical integration...} \end{array}$$

$$\left\{ \begin{array}{l} p_r = ? \\ p_\theta = ? \end{array} \right. \quad (1)$$

Trajectories in phase space: (a,b,d) are Lennard-Jones systems of about 100 particles, (c) is liquid water (DFT forces, 300K). (a) is crystal, (b) is gas, (c) is hydrogen (first panel) and oxygen (second panel) of liquid water, (d) shows the melting of a Lennard-Jones crystal (initially crystal, in the end quite liquid).

Euler-Lagrange:

$$L = K - U = \frac{m(\dot{x}^2 + \dot{y}^2)}{2} + \frac{k}{r}$$

some work!

$$= \dots = \frac{m}{2}(r^2 + r^2\dot{\theta}^2) + \frac{k}{r}$$

effort: convoluting K
(well worth)

$$\delta \int_A^B L dt = 0 \dots \Rightarrow \frac{d}{dt} \left(\frac{\partial L}{\partial \dot{q}} \right) = \frac{\partial L}{\partial q} \quad \text{for any } q$$

$$\left\{ \frac{d}{dt} \left(\frac{\partial L}{\partial \dot{r}} \right) = m\ddot{r} = \frac{\partial L}{\partial r} = m r \dot{\theta}^2 - \frac{k}{r^2} \right.$$

\uparrow
 r^2/mr^3

$$\left. \frac{d}{dt} \left(\frac{\partial L}{\partial \dot{\theta}} \right) = \frac{d}{dt} (mr^2\dot{\theta}) = \frac{\partial L}{\partial \theta} = 0 \quad l = \text{const.} \right.$$

careful:

use formally
and strictly
 $r, \dot{r}, \theta, \dot{\theta}$ as
indep. variables!
(Same for H's eq.)

$$\rightarrow \text{H's eq. : } p_q = \frac{\partial L}{\partial \dot{q}}, \text{ here } p_r = \frac{\partial L}{\partial \dot{r}} = m\dot{r} \quad (\text{intuitive})$$

$$H = \frac{p_r^2}{2m} + \frac{p_\theta^2}{2mr^2} - \frac{k}{r} \quad p_\theta = \frac{\partial L}{\partial \dot{\theta}} = mr^2\dot{\theta} = l \quad (\text{not so intuitive...})$$

$$\begin{cases} \dot{r} = \frac{\partial H}{\partial p_r} = \\ \dot{p}_r = \frac{\partial H}{\partial r} = \\ \dot{\theta} = \frac{\partial H}{\partial p_\theta} = \\ \dot{p}_\theta = -\frac{\partial H}{\partial \theta} = 0 \end{cases} \quad \begin{aligned} & \dot{r} = \frac{\partial H}{\partial p_r} = p_r/m \\ & \dot{p}_r = -\frac{\partial H}{\partial r} = p_\theta^2/mr^3 - k/r^2 \\ & \dot{\theta} = \frac{\partial H}{\partial p_\theta} = p_\theta/mr^2 \\ & \dot{p}_\theta = -\frac{\partial H}{\partial \theta} = 0 \end{aligned}$$

$p_\theta = l = \text{const}$
 $\dot{\theta} = \text{const}$
etc.

Take-home message: we made effort to write K with \vec{P} ,
then we have general form of e.o.m.

(2)

Phase space: a nice place to work in SP (Liouville, eapp...)
 (also for QM)

$$\ddot{x} = -\omega^2 x : \quad x(t) = a \cos \omega t + b \sin \omega t$$

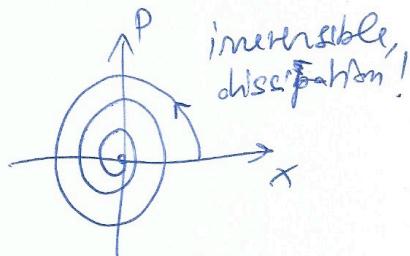
$$\dot{x}(0) = 0 \Rightarrow x = x_0 \cos \omega t$$

$$\dot{x} = -x_0 \omega \sin \omega t$$

$$\dot{p} = -m x_0 \omega \sin \omega t$$

add damping: $\ddot{x} = -\gamma \dot{x} - \omega^2 x$

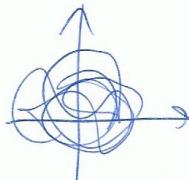
\uparrow
 non-Hamiltonian,
 it is not from H applying H's eq.



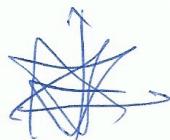
many coupled osc.: nice numerical study, great
 check also online...

atom in liquid:

(ask students
 to guess!)



atom in gas:



TIME EVOL. OF OBSERVABLES

Obs is in general $A(q, p, t)$, commonly $A(q, p)$

(e.g. density in a region, or average momentum, or $g(r)$...)
 (how can it "not be" a function of q, p ??)

$$A = A(q(t), p(t)) \Rightarrow \frac{dA}{dt} = \frac{\partial A}{\partial q} \dot{q} + \frac{\partial A}{\partial p} \dot{p} = \frac{\partial A}{\partial q} \frac{\partial H}{\partial p} - \frac{\partial A}{\partial p} \frac{\partial H}{\partial q} = \{A, H\}$$

$$A = f(H) \Rightarrow \frac{dA}{dt} = \frac{\partial A}{\partial H} \left(\frac{\partial H}{\partial q} \frac{\partial H}{\partial p} - \frac{\partial H}{\partial p} \frac{\partial H}{\partial q} \right) = 0 \quad A \text{ is time-indep!} \quad \textcircled{3}$$

Now in QM: $i\hbar |\dot{\psi}\rangle = H |\psi\rangle$

$$|\psi(0)\rangle = \sum_{\alpha} c_{\alpha} |\alpha\rangle \quad \text{with} \quad H |\alpha\rangle = E_{\alpha} |\alpha\rangle \Rightarrow$$

$$|\psi(t)\rangle = \frac{H}{i\hbar} |\psi(0)\rangle \quad \xrightarrow{\text{Schrödinger Eqn.}} \quad |\psi(t)\rangle = e^{-iHt/\hbar} |\psi(0)\rangle \\ = \left(1 - \frac{iHt}{\hbar} + \frac{1}{2} \left(-\frac{iHt}{\hbar}\right)^2 + \dots\right) |\psi(0)\rangle$$

$$= e^{-iHt/\hbar} \sum_{\alpha} c_{\alpha} |\alpha\rangle = \sum_{\alpha} c_{\alpha} e^{-iE_{\alpha}t/\hbar} |\alpha\rangle$$

time evol.

dictated by E , like in
classical mech ...

$$\langle E \rangle = \langle \psi | H | \psi \rangle = \sum_{\alpha} |c_{\alpha}|^2 E_{\alpha} = \sum_{\alpha, \beta} c_{\alpha}^* e^{iE_{\alpha}t/\hbar} \langle \alpha | H | \beta \rangle c_{\beta} e^{-iE_{\beta}t/\hbar} \\ = \dots$$

$$\langle A \rangle = \langle \psi(t) | A | \psi(t) \rangle$$

$$\begin{aligned} \frac{d\langle A \rangle}{dt} &= \langle \dot{\psi} | A | \psi \rangle + \langle \psi | \dot{A} | \psi \rangle + \langle \psi | A | \dot{\psi} \rangle \\ &= -\frac{1}{i\hbar} \langle \psi | HA | \psi \rangle + \frac{\partial \langle A \rangle}{\partial t} + \langle \psi | A H | \psi \rangle \frac{1}{i\hbar} \\ &= \frac{1}{i\hbar} \langle [A, H] \rangle + \langle \frac{\partial A}{\partial t} \rangle \end{aligned}$$

Once again, if $\frac{\partial A}{\partial t} = 0$ & $[A, H] = 0$ A is time-indep.

$$A = f(H) \Rightarrow \frac{d\langle A \rangle}{dt} = \frac{d}{dt} \left(\int dE f(E) \langle E | A | E \rangle \right) \xrightarrow{\text{because } [f(H), H] = 0} \quad \textcircled{4}$$

$f(H) |\alpha\rangle = f(E_{\alpha}) |\alpha\rangle$
 $\frac{\partial A}{\partial t} = \frac{\partial}{\partial t} \langle E | A | E \rangle$ because $f(H)$ & H commute!

TD2

Ex. 1: multivariate calculus, exact vs inexact differentials

Taken from Ref. [1] pages 109–111 ("mathematical background 2"):

Mathematical background 2 Multivariate calculus

A thermodynamic property of a system typically depends on a number of variables, such as the internal energy depending on the amount, volume, and temperature. To understand how these properties vary with the conditions we need to understand how to manipulate their derivatives. This is the field of multivariate calculus, the calculus of several variables.

MB2.1 Partial derivatives

A partial derivative of a function of more than one variable, such as $f(x,y)$, is the slope of the function with respect to one of the variables, all the other variables being held constant (Fig. MB2.1). Although a partial derivative shows how a function changes when one variable changes, it may be used to determine how the function changes when more than one variable changes by an infinitesimal amount. Thus, if f is a function of x and y , then when x and y change by dx and dy , respectively, f changes by

$$df = \left(\frac{\partial f}{\partial x} \right)_y dx + \left(\frac{\partial f}{\partial y} \right)_x dy \quad (\text{MB2.1})$$

where the symbol ∂ ('curly d') is used (instead of d) to denote a partial derivative and the subscript on the parentheses indicates which variable is being held constant. The quantity df is also called the differential of f . Successive partial derivatives may be taken in any order:

$$\left(\frac{\partial}{\partial y} \left(\frac{\partial f}{\partial x} \right)_y \right)_x = \left(\frac{\partial}{\partial x} \left(\frac{\partial f}{\partial y} \right)_x \right)_y, \quad (\text{MB2.2})$$

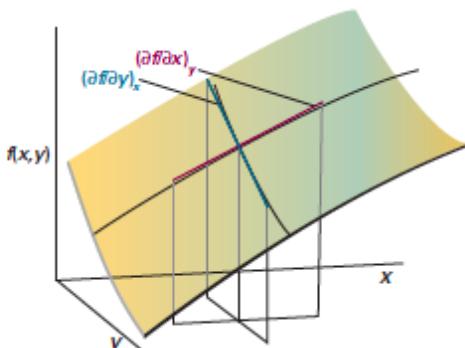


Figure MB2.1 A function of two variables, $f(x,y)$, as depicted by the coloured surface and the two partial derivatives, $(\partial f / \partial x)_y$ and $(\partial f / \partial y)_x$, the slope of the function parallel to the x - and y -axes, respectively. The function plotted here is $f(x,y) = ax^3y + by^2$ with $a=1$ and $b=-2$.

Brief illustration MB2.1 Partial derivatives

Suppose that $f(x,y) = ax^3y + by^2$ (the function plotted in Fig. MB2.1) then

$$\left(\frac{\partial f}{\partial x} \right)_y = 3ax^2y \quad \left(\frac{\partial f}{\partial y} \right)_x = ax^3 + 2by$$

Then, when x and y undergo infinitesimal changes, f changes by

$$df = 3ax^2y dx + (ax^3 + 2by)dy$$

To verify that the order of taking the second partial derivative is irrelevant, we form

$$\begin{aligned} \left(\frac{\partial}{\partial y} \left(\frac{\partial f}{\partial x} \right)_y \right)_x &= \left(\frac{\partial (3ax^2y)}{\partial y} \right)_x = 3ax^2 \\ \left(\frac{\partial}{\partial x} \left(\frac{\partial f}{\partial y} \right)_x \right)_y &= \left(\frac{\partial (ax^3 + 2by)}{\partial x} \right)_y = 3ax^2 \end{aligned}$$

In the following, z is a variable on which x and y depend (for example, x , y , and z might correspond to p , V , and T).

Relation 1. When x is changed at constant z :

$$\left(\frac{\partial f}{\partial x} \right)_z = \left(\frac{\partial f}{\partial x} \right)_y + \left(\frac{\partial f}{\partial y} \right)_x \left(\frac{\partial y}{\partial x} \right)_z \quad (\text{MB2.3a})$$

Relation 2

$$\left(\frac{\partial y}{\partial x} \right)_z = \frac{1}{(\partial x / \partial y)_z} \quad (\text{MB2.3b})$$

Relation 3

$$\left(\frac{\partial x}{\partial y} \right)_z = - \left(\frac{\partial x}{\partial z} \right)_y \left(\frac{\partial z}{\partial y} \right)_x \quad (\text{MB2.3c})$$

By combining Relations 2 and 3 we obtain the Euler chain relation:

$$\left(\frac{\partial y}{\partial x} \right)_z \left(\frac{\partial x}{\partial z} \right)_y \left(\frac{\partial z}{\partial y} \right)_x = -1 \quad \text{Euler chain relation} \quad (\text{MB2.4})$$

MB2.2 Exact differentials

The relation in eqn MB2.2 is the basis of a test for an exact differential; that is, the test of whether

$$df = g(x,y)dx + h(x,y)dy \quad (\text{MB2.5})$$

has the form in eqn MB2.1. If it has that form, then g can be identified with $(\partial f/\partial x)$, and h can be identified with $(\partial f/\partial y)_x$. Then eqn MB2.2 becomes

$$\left(\frac{\partial g}{\partial y}\right)_x = \left(\frac{\partial h}{\partial x}\right)_y$$

Test for exact differential

(MB2.6)

Brief illustration MB2.2 Exact differentials

Suppose, instead of the form $df = 3ax^2ydx + (ax^3 + 2by)dy$ in the previous *Brief illustration*, we were presented with the expression

$$df = \overbrace{3ax^2y}^{g(x,y)} dx + \overbrace{(ax^2 + 2by)}^{h(x,y)} dy$$

with ax^2 in place of ax^3 inside the second parentheses. To test whether this is an exact differential, we form

$$\begin{aligned}\left(\frac{\partial g}{\partial y}\right)_x &= \left(\frac{\partial(3ax^2y)}{\partial y}\right)_x = 3ax^2 \\ \left(\frac{\partial h}{\partial x}\right)_y &= \left(\frac{\partial(ax^2 + 2by)}{\partial x}\right)_y = 2ax\end{aligned}$$

These two expressions are not equal, so this form of df is not an exact differential and there is not a corresponding integrated function of the form $f(x,y)$.

If df is exact, then we can do two things:

- From a knowledge of the functions g and h we can reconstruct the function f .
- Be confident that the integral of df between specified limits is independent of the path between those limits.

The first conclusion is best demonstrated with a specific example.

Brief illustration MB2.3 The reconstruction of an equation

We consider the differential $df = 3ax^2ydx + (ax^3 + 2by)dy$, which we know to be exact. Because $(\partial f/\partial x)_y = 3ax^2y$, we can integrate with respect to x with y held constant, to obtain

$$f = \int df = \int 3ax^2y dx = 3ay \int x^2 dx = ax^3y + k$$

where the 'constant' of integration k may depend on y (which has been treated as a constant in the integration), but not on x . To find $k(y)$, we note that $(\partial f/\partial y)_x = ax^3 + 2by$, and therefore

$$\left(\frac{\partial f}{\partial y}\right)_x = \left(\frac{\partial(ax^3y + k)}{\partial y}\right)_x = ax^3 + \frac{dk}{dy} = ax^3 + 2by$$

Therefore

$$\frac{dk}{dy} = 2by$$

from which it follows that $k = by^2 + \text{constant}$. We have found, therefore, that

$$f(x,y) = ax^3y + by^2 + \text{constant}$$

which, apart from the constant, is the original function in the *Brief illustration* MB2.1. The value of the constant is pinned down by stating the boundary conditions; thus, if it is known that $f(0,0) = 0$, then the constant is zero.

To demonstrate that the integral of df is independent of the path is now straight forward. Because df is a differential, its integral between the limits a and b is

$$\int_a^b df = f(b) - f(a)$$

The value of the integral depends only on the values at the end points and is independent of the path between them. If df is not an exact differential, the function f does not exist, and this argument no longer holds. In such cases, the integral of df does depend on the path.

Brief illustration MB2.4 Path-dependent integration

Consider the inexact differential (the expression with ax^2 in place of ax^3 inside the second parentheses):

$$df = 3ax^2ydx + (ax^2 + 2by)dy$$

Suppose we integrate df from $(0,0)$ to $(2,2)$ along the two paths shown in Fig. MB2.2. Along Path 1,

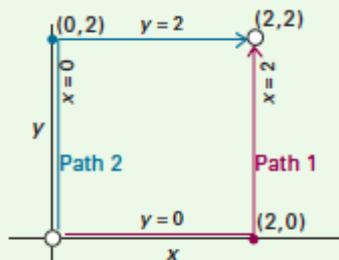


Figure MB2.2 The two integration paths referred to in *Brief illustration* MB2.4.

$$\begin{aligned}\int_{\text{Path 1}} df &= \int_{0,0}^{2,0} 3ax^2y \, dx + \int_{2,0}^{2,2} (ax^2 + 2by) \, dy \\ &= 0 + 4a \int_0^2 y \, dy + 2b \int_0^2 y \, dy = 8a + 4b\end{aligned}$$

whereas along Path 2,

$$\begin{aligned}\int_{\text{Path 2}} df &= \int_{0,2}^{2,2} 3ax^2y \, dx + \int_{0,0}^{0,2} (ax^2 + 2by) \, dy \\ &= 6a \int_0^2 x^2 \, dx + 0 + 2b \int_0^2 y \, dy = 16a + 4b\end{aligned}$$

The two integrals are not the same.

An inexact differential may sometimes be converted into an exact differential by multiplication by a factor known as an *integrating factor*. A physical example is the integrating factor $1/T$ that converts the inexact differential dq_{rev} into the exact differential dS in thermodynamics (Topic 3A).

Brief illustration MB2.5 An integrating factor

We have seen that the differential $df = 3ax^2y \, dx + (ax^2 + 2by) \, dy$ is inexact; the same is true when we set $b=0$ and consider $df = 3ax^2y \, dx + ax^2 \, dy$ instead. Suppose we multiply this df by $x^m y^n$ and write $x^m y^n df = df'$, then we obtain

$$df' = \underbrace{3ax^{m+2}y^{n+1}}_{g(x,y)} \, dx + \underbrace{ax^{m+2}y^n}_{h(x,y)} \, dy$$

We evaluate the following two partial derivatives:

$$\begin{aligned}\left(\frac{\partial g}{\partial y}\right)_x &= \left(\frac{\partial(3ax^{m+2}y^{n+1})}{\partial y}\right)_x = 3a(n+1)x^{m+2}y^n \\ \left(\frac{\partial h}{\partial x}\right)_y &= \left(\frac{\partial(ax^{m+2}y^n)}{\partial x}\right)_y = a(m+2)x^{m+1}y^n\end{aligned}$$

For the new differential to be exact, these two partial derivatives must be equal, so we write

$$3a(n+1)x^{m+2}y^n = a(m+2)x^{m+1}y^n$$

which simplifies to

$$3(n+1)x = m+2$$

The only solution that is independent of x is $n=-1$ and $m=-2$. It follows that

$$df' = 3adx + (a/y)dy$$

is an exact differential. By the procedure already illustrated, its integrated form is $f'(x,y) = 3ax + a \ln y + \text{constant}$.

TD2

1) Multivariate calculus (nice demonstrations: Allen app. A)

$$f(x,y,z) \sim df =$$

1.1, 1.2

$f(x, y)$, $x(z)$, $y(z)$:

$$df = \frac{\partial f}{\partial x} \left(\frac{\partial x}{\partial z} \right)_y dx + \left(\frac{\partial f}{\partial y} \right)_x dy \quad dx = \frac{dx}{dz} dz, \quad dy = \frac{dy}{dz} dz$$

$$\frac{df}{dz} = \left(\frac{\partial f}{\partial x} \right)_y \frac{dx}{dz} + \left(\frac{\partial f}{\partial y} \right)_x \frac{dy}{dz}$$

$$df = \frac{df}{dz} dz$$

$$d\psi = \left(\frac{\partial \psi}{\partial x} \right)_{yz} dx + \left(\frac{\partial \psi}{\partial y} \right)_{xz} dy + \left(\frac{\partial \psi}{\partial z} \right)_{xy} dz$$

but $z = z(x, y)$

now we fix z : $dz = 0$,

$$(df)_z = \left(\frac{\partial f}{\partial x} \right)_{yz} dx + \left(\frac{\partial f}{\partial y} \right)_{xz} dy \quad \text{we divide by } dx:$$

$$\left(\frac{\partial f}{\partial x} \right)_z = \left(\frac{\partial f}{\partial x} \right)_{yz} + \left(\frac{\partial f}{\partial y} \right)_{xz} \left(\frac{\partial y}{\partial x} \right)_z$$

↑
we do not
fix y

↑
more pedantic
notation than

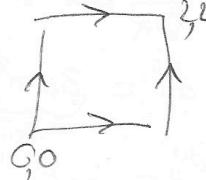
Atkins, we specify
that z is fixed...

relations like $z = z(x, y)$ usually come from $f(x, y, z) = \text{const}$
see Allen! (1)

If we integrate the inexact

$$df = 3ax^2y \, dx + (ax^2 + 2by) \, dy \text{ from } (0,0) \text{ to } (2,2)$$

along 2 paths we get different results:



ANSWER

1.5) ~~df above can become exact with int. factor:~~

$$df = 3ax^2y \, dx + ax^2 \, dy \text{ is inexact,}$$

let's consider

$$df' = df \times^{m+n} = \underbrace{3ax^{m+2}y^{n+1}}_g \, dx + \underbrace{ax^{m+2}y^n}_h \, dy$$

$$\frac{\partial g}{\partial y} = 3a(n+1)x^{m+2}y^n := \frac{\partial h}{\partial x} = a(m+2)x^{m+1}y^n$$

$$\Rightarrow 3(n+1)x = m+2 \quad \forall x : \quad n=-1, \quad m=-2 \rightarrow$$

$$df' = 3ax \, dx + a y^{-1} \, dy$$

~~~ integration procedure:  $f' = 3ax + a \ln y + c$ .

□

13)  $df = g(x,y)dx + h(x,y)dy$  : exact if  $\frac{\partial g}{\partial y} = \frac{\partial h}{\partial x}$   
 $\stackrel{?}{=} \frac{\partial f}{\partial x} dx + \frac{\partial f}{\partial y} dy$ ?

test:  $df = \underbrace{3ax^2y}_{g} dx + \underbrace{(ax^2+2by)}_{h} dy$  is exact?

$$\frac{\partial g}{\partial y} = 3ax^2 \neq \frac{\partial h}{\partial x} = 2ax \text{ not exact!}$$

14) If  $df$  is exact  $\rightarrow$  from  $g, h$  we reconstruct  $f$   
 $\int_1^2 df = \Delta F$  does not depend on path

ex:  $f = ax^3y + by^2$

$$f = \int df = \int \left( \frac{\partial f}{\partial x} \right)_y dx = \int dx 3ax^2y = 3ay \int x^2 dx = ax^3y + k$$

$k$  can depend on  $y$  (that was treated as const. during integration) but not on  $x$ . Let's find  $k(y)$ :

$$\left( \frac{\partial f}{\partial y} \right)_x = ax^3 + 2by = \frac{\partial}{\partial y} (ax^3y + k)_x = ax^3 + \frac{\partial k}{\partial y}$$

$$\text{so } 2by = \frac{\partial k}{\partial y}, \quad k = by^2 + c \quad (\text{same } f \text{ as in 1st ex})$$

To define  $c$  we need boundary cond., e.g.  $f(0,0)=0$ .

Since  $df$  is exact, by def.  $\int_1^2 df = f(2) - f(1)$  does not depend on path.

Show examples like  $c = \partial E / \partial T$ ,  $1/c = \partial T / \partial E$  with different forms of  $E(T)$ : direct calculation and change of variable in the end.

Nice explanations: Walter Appel "mathématiques pour la physique" pag. 575

## Ex. 2: Conditions of equilibrium and equations of state

Taken from Callen ch. 2. We saw that  $E = E(S, V, N)$  ( $N$  can be a vector) is a state function,

$$dE = \frac{\partial E}{\partial S} dS + \frac{\partial E}{\partial V} dV + \frac{\partial E}{\partial N} dN \equiv T dS - p dV + \mu dN \equiv \delta Q + \delta W_M + \delta W_C$$

(note that, in absence of work,  $dS = \delta Q/T$  so dividing heat by temperature makes it an exact differential,  $1/T$  is an integrating factor, see connection with ex. 1).  $T, p, \mu$  are derivatives of a function of  $S, V, N$ , so they are functions of the same variables:  $T(S, V, N)$ ,  $p(S, V, N)$ ,  $\mu(S, V, N)$ . Such functions, connecting intensive parameters with extensive ones, are called "equations of state" (EOS). Knowing all these EOS is equivalent to knowing the fundamental equation (i.e., the form of  $E$  or  $S$ ), which contains all TD information. See connection with ex. 1.

XXX tricky point: explain why  $E$  is a function of  $S$ , not obvious from intuition.

$E$  and  $S$  are homogeneous first order:  $E(\lambda S, \lambda V, \lambda N) = \lambda E(S, V, N)$  and likewise for  $S$ . Thus energy and entropy are extensive, then their derivatives must be intensive, e.g.,  $T(\lambda S, \lambda V, \lambda N) = T(S, V, N)$ : demonstrate using

$$\frac{\partial}{\partial(ax)} = \frac{1}{a} \frac{\partial}{\partial x}$$

where  $a$  is any constant. Formally, if we call  $x_1, x_2, x_3, \dots$  the extensive parameters  $V, N_1, N_2, \dots$ , and  $P_j = \partial E / \partial x_j$  we can write

$$dE = T dS + \sum P_j dx_j$$

which is called energy representation. Likewise, we can use the entropy representation (with  $F_j = \partial S / \partial x_j$ )

$$dS = \frac{1}{T} dE + \sum F_j dx_j$$

One can directly invert the fundamental relation  $dE = T dS - p dV + \mu dN$  to get the other fundamental relation

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

that clearly shows how  $F_j = -P_j/T$ . Even though the energy and entropy representations are equivalent, note that the variables change:  $P_j(S, V, N)$  versus  $F_j(E, V, N)$ . Therefore it is important to specify which parameters are kept fixed while computing partial derivatives, otherwise a great confusion arises!

Optional (they already saw in L2): demonstrate that, at equilibrium, when two subsystems exchange only heat one gets  $T_1 = T_2$  from the maximization of  $S$ . Also, if initially  $T_1 > T_2$ , relaxation to equilibrium being irreversible ( $\Delta S > 0$ ) results in heat flow from hot to cold.

Similarly one can demonstrate that  $p_1 = p_2$  and  $\mu_1 = \mu_2$  at equilibrium.

## Ex. 3: correct and incorrect fundamental equations (home exercise)

Other nice exercises on the fundamental equations are the series Callen 2.2-x.

$$a) S = \left( \frac{R^2}{U_0 \theta} \right)^{1/3} (NVU)^{1/3} \stackrel{\text{TD2 ex3}}{=} C (NVU)^{1/3}, U = \frac{S^3}{C^3 NV}$$

$$\textcircled{(iii)} S(2N, 2V, 2U) = C (8NVU)^{1/3} = 2C(NVU)^{1/3} \quad \text{ok!}$$

(S grows with U)

$$T = \frac{\partial U}{\partial S}, \frac{1}{T} = \frac{\partial S}{\partial U} = C^{1/3} U^{-2/3}; U = C'' S^3, \frac{\partial U}{\partial S} = 3C'' S^2 = T$$

$T \rightarrow 0, \frac{1}{T} \rightarrow \infty$

$$= \frac{C^3 S^3}{NV}, T = \frac{3S^3}{C^3 NV}$$

$$T = \frac{\partial U}{\partial S} = \frac{3S^2}{C^3 NV} = \frac{3C^2 (NVU)^{2/3}}{C^3 NV} = \frac{3U^{2/3}}{C(NV)^{1/3}}$$

$\frac{1}{T} = \frac{\partial S}{\partial U} = C(NV)^{1/3} U^{-2/3}$

} ok!

$$\textcircled{(iv)} S=0 \text{ at } T=0: T=0 \Rightarrow U=0 \Rightarrow S=0 \quad \boxed{\text{ok!}}$$

$$b) S = C \left( \frac{NU}{V} \right)^{2/3}, U = \left( \frac{S}{C} \right)^{3/2} \frac{V}{N}$$

$$\textcircled{(v)} S(2N, 2V, 2U) = C \left( 2 \frac{NU}{V} \right)^{2/3} = 2^{2/3} S(NVU) \quad \boxed{\text{wrong No.}}$$

$$\textcircled{(vi)} S = C \left( NU + DV^2 \right)^{1/2} \xrightarrow{\text{always } > 0}$$

condition for all equil states?

$$\textcircled{(vii)} S(2N, 2V, 2U) = C \left( 4NU + 4DV^2 \right)^{1/2} = 2S(N, V, U) \quad \text{ok!}$$

$$\textcircled{(viii)} U = \frac{S^2}{C^2} - DV^2, T = \frac{\partial U}{\partial S} = \frac{2S}{C^2}, T=0 \Rightarrow S=0 \quad \boxed{\text{ok!}}$$

(S grows with U)

[ $\textcircled{(ii)}$ : S must be def. for all equil states, i.e. any  
arbitrary shift. let's say  $U > \cancel{U}$ ]  $\sqrt{5}$

c)  $S = C(NU + DV^2)^{1/2}$   
 $NU + DV^2 > 0$  always!

d)  $S = C \frac{V^3}{NU}$      $S(2N, 2V, 2U) = C \frac{8V}{4NU} = 2S(NVU)$  ok!  
 $U = C \frac{V^3}{NS}$ ,  $T = \frac{\partial U}{\partial S} = -C \frac{V^3}{NS^2}$   $\begin{matrix} < 0 \text{ and it} \\ \text{decreases} \\ \text{with } S, \end{matrix}$  wrong!  
(III)

e)  $S = C(N^2 VU^2)^{1/5}$ ,  $S(2N, 2V, 2U) = C(2^5 N^2 VU^2)^{1/5} = 2S(NVU)$  ok!

$$U = \sqrt[5]{\left(\frac{S}{C}\right)^5 \frac{1}{N^2 V}} = \left(\frac{S}{C}\right)^{5/2} \frac{1}{N\sqrt{V}}, T = \frac{\partial U}{\partial S} = \frac{5}{2} \frac{S^{3/2}}{C^{5/2}} \frac{1}{N\sqrt{V}} \quad \text{ok!}$$

$T \rightarrow 0, S \rightarrow 0$ : ok!

f)  $S = NR \log\left(\frac{UV}{CN^2}\right)$  #,  $S(2N, 2V, 2U) = 2NR \log\left(\frac{4UV}{C4N^2}\right) = 2S(NVU)$  ok

$$\frac{UV}{CN^2} = e^{S/NR}, U = \frac{CN^2}{V} e^{S/NR}, T = \frac{\partial U}{\partial S} = \frac{CN}{RV} e^{S/NR}$$

it grows with  $S$ , but for ~~for  $S \rightarrow 0$~~   $S \rightarrow 0$   $T \rightarrow 0$ !

$$\frac{1}{T} = \frac{\partial S}{\partial U} = \frac{NR}{V}, T = \frac{U}{NR} \quad \text{ok}$$

g)  $S = C\sqrt{NU} e^{-V^2/2DN^2}$ ,  $S(2N, 2V, 2U) = C2\sqrt{NU} e^{-V^2/2DN^2}$  ok  
 $\approx 2S(NVU)$

$$\frac{1}{T} = \frac{\partial S}{\partial U} = +\frac{C\sqrt{N}}{2\sqrt{U}} e^{-V^2/2DN^2}, U = \frac{S^2}{C^2 N} e^{V^2/2DN^2}, T = \frac{\partial U}{\partial S} = \frac{2S}{C^2 N} e^{V^2/2DN^2}$$

$$T = \frac{2\sqrt{U}}{C^2 N} e^{V^2/2DN^2}, \sqrt{U} = \frac{S}{C\sqrt{N}} e^{V^2/2DN^2}, T = \frac{2S}{C^2 N} e^{V^2/2DN^2} \quad \boxed{\text{ok!}}$$

$$h) S = C \sqrt{NV} e^{-UV/NR}, S(2N, 2V, 2U) = 2C \sqrt{NV} e^{-2UV/NR}$$

$$i) U = C \frac{S^2}{V} e^{S/NR} \neq 2U(NVU) \quad \underline{\text{wrong!}}$$

$$U(2S, 2N, 2V) = 2C \frac{S^2}{V} e^{S/NR} = 2U(NVU) \quad \text{ok!}$$

$$\begin{aligned} T &= \frac{\partial U}{\partial S} = 2C \frac{S}{V} e^{S/NR} + C \frac{S^2}{V} \frac{1}{NR} e^{S/NR} \\ &= \frac{C}{V} e^{S/NR} \left( 2S + \frac{S^2}{NR} \right) \geq 0, \quad S \rightarrow 0: T \rightarrow 0 \quad \boxed{\text{ok!}} \end{aligned}$$

$$j) U = C NV \left( 1 + \frac{S}{NR} \right) e^{-S/NR}$$

$$U(2N, 2V, 2S) = 4C NV \left( 1 + \frac{S}{NR} \right) e^{-S/NR} \neq 2U(NVU) \quad \underline{\text{wrong!}}$$

# TD3

## Ex. 1: constructing the entropy of the ideal gas from TD

Follow Brunet section 3.3.3: from  $PV = nRT$  and  $E = (3/2)nRT$  one can write  $S$ , after some guesswork about the chemical potential based on extensivity of  $S$ .

## Ex. 1: Soft approach to Sackur-Tetrode entropy

Sketch, semi-qualitatively, path to Sackur-Tetrode formula for ideal gas, considering ratios of numbers of microstates rather than absolute number. Start comparing different energies, for fixed  $V, N$ :

$$\frac{\Omega_2}{\Omega_1} = \frac{\int_{\sum p_i^2/2m=E_2} d^{3N}p}{\int_{\sum p_i^2/2m=E_1} d^{3N}p} = \frac{\int d^{3N}p \delta(\sqrt{\sum p_i^2} - \sqrt{2mE_2})}{\int d^{3N}p \delta(\sqrt{\sum p_i^2} - \sqrt{2mE_1})}$$

Where we formally realize the constant-energy constraint in the integral domain using Dirac  $\delta$  functions (rather, generalized functions, or distributions). Some properties from Dirac's book on QM:

There are a number of elementary equations which one can write down about  $\delta$  functions. These equations are essentially rules of manipulation for algebraic work involving  $\delta$  functions. The meaning of any of these equations is that its two sides give equivalent results as factors in an integrand.

Examples of such equations are

$$\delta(-x) = \delta(x) \quad (6)$$

$$x\delta(x) = 0, \quad (7)$$

$$\delta(ax) = a^{-1}\delta(x) \quad (a > 0), \quad (8)$$

$$\delta(x^2 - a^2) = \frac{1}{2}a^{-1}\{\delta(x-a) + \delta(x+a)\} \quad (a > 0), \quad (9)$$

$$\int \delta(a-x) dx \delta(x-b) = \delta(a-b), \quad (10)$$

$$f(x)\delta(x-a) = f(a)\delta(x-a). \quad (11)$$

Note: in the calculation above of  $\Omega_2/\Omega_1$  we used  $\delta(\sqrt{\sum p_i^2} - \sqrt{2mE})$  instead of  $\delta(\sum p_i^2 - 2mE)$ : the former selects the hypersphere surface in the integral, the latter is a bit different, it has units of 1/momentum<sup>2</sup>, but it can also be used, as Tuckerman does, especially given eq. 9 here above in Dirac's book.

We get a feeling from what happens in 1D, 2D, 3D...

$$\begin{aligned} \int_{-\infty}^{\infty} dx \delta(|x| - R) &= 2, \\ \int dx \int dy \delta(\sqrt{x^2 + y^2} - R) &= \int d\theta \int dr r \delta(r - R) = 2\pi R, \\ \int dr \int d\theta \int d\phi r^2 \sin(\theta) \delta(r - R) &= 4\pi R^2 \end{aligned}$$

and so on, so the integral  $\propto R^{d-1}$ , and we can infer

$$\frac{\Omega_2}{\Omega_1} = \frac{\sqrt{2mE_2}^{3N-1}}{\sqrt{2mE_1}^{3N-1}} \approx \left(\frac{E_2}{E_1}\right)^{3N/2}$$

where we discard "-1" in the exponent for large  $N$ , the argument being that in  $S$  we discard all non-extensive parts. This grows very quickly, exponentially with  $N$ , similar to the result in CM3 where for varying volumes we got  $(V_2/V_1)^N$  (this can be also obtained from  $\Omega_2/\Omega_1$  fixing  $N, E$ ). So far we can try to deduce

$$\Omega(N, V, E) \approx V^N E^{3N/2} f,$$

$$S = k \log \Omega \approx Nk \left( \log V + \frac{3}{2} \log E + \dots \right)$$

Here, the function  $f$  could be determined by explicitly considering variations in the number of particles. Can you deduce, at least in part, the missing term from the requirement of extensive  $S$ ?

The complete calculation gives Sackur-Tetrode formula:

$$S \approx Nk \left( \frac{5}{2} + \log \frac{V}{N} + \frac{3}{2} \log \frac{4\pi m E}{3Nh^2} \right)$$

(it contains a factor  $N!$  to account for indistinguishability of particles, whether quantum or classic, e.g. colloids... a long story). Check that it is extensive, and compute derivatives w.r.t.  $E, V, N$ , giving  $T, p, \mu$ . Are the latter intensive? Now we have a definite example where to apply the methods of TD2. Note how the relation can be inverted to give  $E(S, V, N)$ , showing explicitly how energy is a function of entropy. A bit cumbersome to understand, but remember that  $S$  is the conjugate variable of  $T$ , and it is more intuitive to think that  $E$  is a function of  $T$ .

The quantity  $\lambda = \sqrt{3Nh^2/4\pi m E}$  is the thermal de Broglie wavelength: explain its intuitive meaning and use it to discuss validity of classical limit.

### Ex. 3: How much entropy is 1 $\mu$ cal?

As an example, raising by  $10^{-6}$  K the temperature of 1 gram of water close to room temperature, i.e., supplying one micro-calorie to the system, a tiny amount of heat, corresponds to  $\Omega_2/\Omega_1 = e^{\Delta S/k} = e^{Q/kT} = e^{10^{15}}$ , a huge increase in number of microstates! Calculation:  $1 \mu\text{cal} = 4.184 \cdot 10^{-6} \text{ J}$ , at room temperature  $kT = 1.38 \cdot 10^{-23} \text{ J/K} \cdot 300 \text{ K} = 4.14 \cdot 10^{-21} \text{ J}$ . Therefore  $\Omega_2/\Omega_1 = \exp[(4.184 \cdot 10^{-6})/(4.14 \cdot 10^{-21})] \approx e^{10^{15}}$ .

$$1) dE = TdS - pdV + \mu dN, \quad dS = \frac{1}{T} dE + \frac{p}{T} dV - \frac{\mu}{T} dN \quad | \text{TD3}$$

$$E = \frac{3}{2} N k T, \quad pV = NkT$$

$$\frac{1}{T} = \frac{3}{2} \frac{Nk}{E}, \quad \frac{p}{T} = \frac{Nk}{V} \rightarrow dS = \underbrace{\frac{3}{2} Nk \frac{dE}{E} + Nk \frac{dV}{V}}_{+} - \frac{\mu}{T} dN$$

$$\text{we miss } \mu: \text{assume first } dN=0, \quad dS = \underbrace{\frac{3}{2} Nk \log E}_{+} + Nk \log V$$

Now  $c = f(N)$  does not depend on  $E, V$

now use extensivity:

$$S(2E, 2V, 2N) = \frac{3}{2} 2Nk \log(E) + 2Nk \log(V) + f(2N)$$

$$= \frac{3}{2} 2Nk \log E + 2Nk \log V + \frac{5}{2} 2Nk \log 2 + f(2N)$$

$$= 2 \left[ \frac{3}{2} Nk \log E + Nk \log V \right] + " \quad " \quad "$$

$$\text{must be } 2S(E, V, N) \rightarrow 2f(N) = \frac{5}{2} 2Nk \log 2 + f(2N)$$

$\lambda$  is arbitrary: if we choose  $\lambda = \frac{1}{N}$  we find

$$\frac{1}{N} f(N) = \frac{5}{2} k \log \frac{1}{N} + f(1), \quad f(N) = N \left( f(1) - \frac{5}{2} k \log N \right)$$

↓  
const indep de  $E, V, N$ ,  
call it  $k_C$ :

$$f(N) = k_N \left( C - \frac{5}{2} \log(N) \right)$$

$$S(E, V, N) = Nk \left[ \frac{3}{2} \log E + \log V - \frac{5}{2} \log N + C \right]$$

$$= Nk \left[ \frac{3}{2} \log \frac{E}{N} + \log \frac{V}{N} + C \right] \quad \text{clearly is extensive.}$$

To know  $C$  we need microscopic calc: stat phys!

$$S = k \log \Omega, \quad \Omega = e^{\frac{S}{k}} \propto \left( \frac{E}{N} \right)^{3N/2} \left( \frac{V}{N} \right)^N = E^{3N/2} V^N N^{-5N/2}$$

$\uparrow$   
we miss  
constant, needed also for dim. reasons  
( $\Omega$  adimensional "number"!)

(1)

2) fix  $N, V$ , vary  $E$ :  $\frac{\Omega_2}{\Omega_1} = \frac{\int d^3p S(E_2 - \sqrt{\sum p_i^2/2m})}{\int d^3p S(E_1 - \sqrt{\sum p_i^2/2m})}$  spherical surfaces  
in  $3N$  dim space

effect of  $\delta$ ?  $\int_{-\infty}^{\infty} dx \delta(|x| - R) = 2$  scales like  $R^0$

1D  $\int_{-\infty}^{\infty} dx \delta(|x| - R) = 2$  scales like  $R^0$

2D  $\int dx dy \delta(\sqrt{x^2 + y^2} - R) = \int_0^{2\pi} d\theta \int_0^\infty dr \delta(r - R) = 2\pi R \propto R^1$

3D  $\int dx dy dz \delta(\sqrt{x^2 + y^2 + z^2} - R) = \int_0^{2\pi} d\theta \int_0^\pi d\varphi \sin \varphi r^2 \delta(r - R) = 4\pi R^2 \propto R^2$

so integrals of delta in  $n$  dim have behavior  $R^{n-1}$  (logical...)

$\rightarrow \frac{\Omega_2}{\Omega_1} = \frac{\int d^3p \delta(\sum p_i^2 - 2mE_2)}{\int d^3p \delta(\sum p_i^2 - 2mE_1)} = \frac{(2mE_2)^{\frac{3N-1}{2}}}{(2mE_1)^{\frac{3N-1}{2}}} = \left(\frac{E_2}{E_1}\right)^{\frac{3N-1}{2}}$

If we fix  $N, E$ :  $\frac{\Omega_2}{\Omega_1} = \frac{\int_{V_2} d^3q}{\int_{V_1} d^3q} = \frac{V_2^N}{V_1^N}$  ↑ but let's remember that  $m$  multiplies  $E$ ...

$\Rightarrow \Omega \propto V^N E^{\frac{3N-1}{2}}$  we neglect "-1" for large  $N$ ...  
↳ we suppress all non-extensive terms in  $S$ !

$S = Nk \log \Omega = Nk \left[ \log V + \frac{3}{2} \log E + \dots \right]$

is not extensive: we need to modify as

$S = Nk \left[ \log \frac{V}{N} + \frac{3}{2} \log \frac{E}{N} + f(N) \right]$

now we are back to same point as ex 1,  
from extensivity we constrain  $f(N)$  and obtain

$S = Nk \left( \log \frac{V}{N} + \frac{3}{2} \log \frac{E}{N} + c \right)$

(2)

$$2.4) S = Nk \left( \frac{5}{2} + \log \frac{V}{N} + \frac{3}{2} \log \left( \frac{4\pi m E}{3N h^2} \right) \right) \quad \text{Sackur-Tetrode}$$

$$S = k \log \Omega = k \log \left[ \frac{\Omega_0}{N!} \right] \quad \text{"discrete nature"}$$

$$\log N! \approx N \log N - N \quad \text{since } dx \approx 1$$

$$\hookrightarrow \sum_1^N \log x \approx \int_1^N \log x \, dx = [x \log x - x]_1^N = N \log N - N + 1$$

$$[\text{more precise: } N! \approx \sqrt{2\pi N} \left( \frac{N}{e} \right)^N \dots]$$

↓  
for small  $N$

$$\approx N \log N - N$$

$$S_D = k \log \Omega + k \log N! \approx k \log \Omega$$

$$Nk \left[ \frac{5}{2} + \log \frac{V}{N} + \frac{3}{2} \log \left( \frac{4\pi m E}{3N h^2} \right) \right] + kN \log N \neq k$$

$$= NK \left[ \frac{3}{2} + \log V + \frac{3}{2} \log \left( \frac{4\pi m E}{3N h^2} \right) \right] \leftarrow \text{not extensive!}$$

$N!$  usually motivated from QM, but it is useful also classically (e.g. collards) if we want  $S$  to be extensive... Also in classical physics  $H$  & observables (macrosc.) are invariant under permutation, subtle...

To do complete derivation of  $S$  we need granularity  $\propto h^{3N}$   
in phase space, volume of hypersphere,  $N!$  counting, approx.  
to keep only extensive parts ( $\propto N$ ) in  $S$ . Too long to do here...

$$2.5) \frac{1}{T} = \frac{\partial S}{\partial E} = \dots = \frac{3}{2} Nk / E$$

$$\frac{P}{T} = \frac{\partial S}{\partial V} = \frac{NK}{V}$$

$$3) -\frac{1}{T} = \frac{\partial S}{\partial N} = \dots \quad \mu = kT \log \left( \frac{N \lambda^3}{V} \right), \quad \lambda = \sqrt{\frac{3N h^2}{4\pi m E}} \quad \text{De Broglie's wavelength}$$

classical limit:  $\lambda^3 \ll \frac{V}{N}$  (no overlap)

so adding particles  $\Rightarrow \frac{N \lambda^3}{V} \ll 1, \mu < 0$

so adding particles in phase space

$$2.6) S = Nk \left[ \frac{5}{2} + \log \frac{V}{N} + \frac{3}{2} \log \left( \frac{4\pi m E}{3N h^2} \right) \right]$$

$$E = ? \quad \frac{S}{Nk} - \frac{5}{2} - \log \frac{V}{N} = \frac{3}{2} \log ( \dots )$$

$$\Rightarrow \frac{4\pi m E}{3N h^2} = \exp \left[ \frac{2}{3} \left( \frac{S}{Nk} - \frac{5}{2} - \log \frac{V}{N} \right) \right]$$

$$E = \frac{3N h^2}{4\pi m} e^{\left[ \frac{2}{3} \left( \frac{S}{Nk} - \frac{5}{2} + \log \frac{V}{N} \right) \right]}$$

it grows with  $S$ , with density, with  $N$ , with  $\frac{1}{m}$

since  $S$  is related to available states in momentum space, higher  $S$  means higher momenta  $\Rightarrow$  higher  $T$ .

Mass-behavior is related to choice of  $q, p$  versus  $q, \dot{q}$ , subtle, see Solyer;

$$E = \frac{1}{2m} \sum p_i^2 \Rightarrow \text{for fixed } E, |p_i| \in [0, \sqrt{2mE}]$$

radius =  $\sqrt{2mE}$  (hypersphere...)

$$E = \frac{m}{2} \sum \dot{q}_i^2 \Rightarrow \text{radius } \sqrt{\frac{2E}{m}} \leftarrow \text{wrong } \frac{1}{m} \text{ behavior!}$$

(since it suggests higher  $m \rightarrow$  lower freedom)

Sacum-Tetradec is right: experimentally, it is verified that  $S_{Kr} - S_{Ar} = \frac{3}{2} Nk \log(m_{Kr}/m_{Ar})$  and not vice-versa.

Very nice: Solyer Ref. 18, 19.

#### **Ex. 4: Guessing entropy by visual inspection**

To relax a bit, show funny example in article of Styer "Insight into entropy", fig. 2,3: test if students are able to predict the most entropic arrangement.

# TD4

1

## TD4 CORRECTIONS

1.1) Sampling with replacements: n° of arrangements =  $N^k$   
 " without "  $N(N-1)\dots(N-k+1)$

■ 6 throws, 6 different faces:

prob. of one specific arrangement with diff. faces

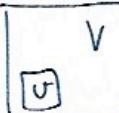
$$\square \square \square \square \square \square = \left(\frac{1}{6}\right)^6 = \frac{1}{6^6}$$

number of permutations =  $6!$

$\Rightarrow$  prob. of any arrangement with diff. faces =  $\frac{6!}{6^6}$

$$= \frac{720}{46656} \approx 1.5\% \quad (\text{we sum prob. of each arrangement})$$

■ prob. different birthdays:  $\frac{N(N-1)\dots(N-M+1)}{N^M}$   $M=23: p < \frac{1}{2}$   $\rightarrow$  10 heads:  $\frac{1}{2^{10}}$

1.2) ■  ideal gas: equal a priori prob. principle in phase space (later courses...)  $\Rightarrow$  also in conf. space

Being in  $V$  ("success") vs being in  $V-V$  ("failure")

$\rightarrow$  Bernoulli trials, exact law is binomial law

$$p(k; n, p) = \binom{n}{k} p^k q^{n-k} = \frac{n!}{k!(n-k)!} p^k q^{n-k}, q = 1-p$$

$$\langle k \rangle = \sum_{k=0}^n \binom{n}{k} k p^k q^{n-k} = p \frac{\partial}{\partial p} \left[ \sum_{k=0}^n \binom{n}{k} p^k q^{n-k} \right] =$$

$$= p \frac{\partial}{\partial p} (p+q)^n = np(p+q)^{n-1} = np \quad (\text{proving also the normalization of the binomial law})$$

(using binomial theorem)

$$\text{Similarly: } \langle k^2 \rangle = \sum_0^n \binom{n}{k} k^2 p^k q^{n-k} = \left( p \frac{\partial}{\partial p} \right)^2 \left[ \sum \dots \right] =$$

$$= p \frac{\partial^2}{\partial p^2} [np(p+q)^{n-1}] = \langle k \rangle^2 + npq, \sigma_k^2 = npq, \frac{\sigma_k}{\langle k \rangle} = \sqrt{\frac{q}{n}} \sqrt{\frac{1}{n}}$$

Note: rel. fluctuations  $\sim \frac{1}{\sqrt{n}}$  is very general law,

(2)

it comes from  $\sigma_s^2 = n \sigma_x^2$  &  $\langle s \rangle = n \langle x \rangle$

whenever  $s = \sum_i^n x_i$  is sum of indep. random variables  
(explanations in the ~~exercises~~ CM4)

→ it explains why macroscopic quantities appear precisely defined (thermodynamics).

■ Thus, prob. to obs.  $k=0$  or  $k=n$  is

$$p(k=0) = \binom{n}{0} p^0 q^n = q^n = \left(\frac{V-v}{V}\right)^n \sim 1 \text{ if } v \ll V$$

$$p(k=n) = \binom{n}{n} p^n q^0 = p^n = \left(\frac{v}{V}\right)^n \sim 0 \quad " "$$

second principle: if we imagine gas initially constrained in  $V$ , and we progressively enlarge box, prob. that it remains in  $V$  becomes quickly ~~as~~ negligible if  $n \gtrsim 10$ , however instantaneous configurations can be observed, with prob.  $p^n$ , that displays all atoms in  $V$ . So, 2<sup>nd</sup> principle is not strictly valid; here we have to be careful, however, in defining "instantaneous  $S$ ", a slippery concept.  $S$  is tightly related to time, it "corresponds" to time spent in a state in the case of metastability (later CMs)... since, in NVE ensemble, system spends equal time in each unit volume of accessible phase space.

$$2.1) \quad \lambda = np \sim 1 : \binom{n}{k} p^k q^{n-k} = \frac{n!}{k!(n-k)!} p^k q^{n-k} \quad (3)$$

$$\approx \frac{n^k}{k!} p^k (1-p)^{n-k} = \frac{(np)^k}{k!} \left(1 - \frac{np}{n}\right)^{n-k}$$

$$= \frac{(np)^k}{k!} \frac{\left(1 - \frac{\lambda}{n}\right)^n}{\left(1 - \frac{\lambda}{n}\right)^k} \quad \text{for fixed } \lambda, \text{ fixed } k,$$

$$\left(1 - \frac{\lambda}{n}\right)^k \rightarrow 0$$

$$\left(1 - \frac{\lambda}{n}\right)^n \rightarrow e^{-\lambda} :$$

prob  $\approx \frac{\lambda^k}{k!} e^{-\lambda}$  (Poisson) but let's remember:  
 $\lambda \sim 1$ ,  $k$  "small"

$$\sum_{k=0}^{\infty} \frac{\lambda^k}{k!} e^{-\lambda} = e^{\lambda} e^{-\lambda} = 1, \quad \langle k \rangle = \sigma_k^2 = \lambda \dots$$

in applications  $\lambda = \tilde{v}t$  (characteristic frequency multiplied by time)  
 $= \tilde{p}V$  (char. density times volume)  
... etc.

hypothesis: random events with constant frequency or density; only 1 parameter!

Poisson is excellent approx. for Binomial for prob. that in a group of  $n=500$  people  $k \ll n$  have birthday on Jan 1<sup>st</sup>:  
 $p = 1/365$ ,  $\lambda = np \approx 1.37 \sim 1$ , Poisson is very similar to binomial for  $k=0, 1, 2, 3 \dots$

2.2) @ HOME: If I look for item on leboncoin,  fixing the distance from an address and buying different addressees I should find the number of results distrib. like Poisson if the density of such item is fixed across France, which is unlikely: more density where there is more population, plus regional differences (more wood in the countryside, more boats on the coast...)

2.3) Moment generating function:  $\langle x^m \rangle = \left. \frac{d^m}{ds^m} \langle e^{sx} \rangle \right|_{s=0}$

$$\blacksquare \text{ binomial: } \langle e^{sx} \rangle = \sum_{k=0}^n \binom{n}{k} e^{sk} p^k q^{n-k}$$

$$(x=k)$$

$$= \sum \binom{n}{k} (e^s p)^k q^{n-k}$$

$$\langle x \rangle = p \sum \left. \binom{n}{k} (e^s p)^{k-1} k q^{n-k} \right|_{s=0} = \sum \binom{n}{k} k p^k q^{n-k}$$

$$= \dots = np$$

$$\langle x^2 \rangle = \dots$$

$$\blacksquare \text{ Poisson: } \langle e^{sx} \rangle = \sum_{k=0}^{\infty} \frac{\lambda^k}{k!} e^{sk} e^{-\lambda} = \sum_{k=0}^{\infty} \frac{(\lambda e^s)^k}{k!} e^{-\lambda}$$

$$\langle x \rangle = \dots = e^{-\lambda} \sum_0^{\infty} \frac{\lambda^k}{k!} \lambda^k = \lambda e^{-\lambda} \sum_1^{\infty} \frac{\lambda^{k-1}}{(k-1)!} = \lambda \sum_0^{\infty} \frac{\lambda^k}{k!} e^{-\lambda} = \lambda$$

$$\begin{aligned} \langle x^2 \rangle &= \dots = \sum_0^{\infty} \frac{k^2 \lambda^k}{k!} e^{-\lambda} = \lambda \sum_0^{\infty} (k-i+1) \frac{\lambda^{k-1}}{(k-i)!} e^{-\lambda} = \\ &= \lambda \sum_0^{\infty} \frac{k-1}{(k-1)!} \lambda^{k-1} e^{-\lambda} + \lambda \sum_1^{\infty} \frac{\lambda^{k-1}}{(k-1)!} e^{-\lambda} = \lambda^2 + \lambda \Rightarrow \sigma_x^2 = \lambda \end{aligned}$$

## MOMENT-GENERATING FUNCTION

Alternative way to compute moments of discrete or continuous dist:

$$\langle e^{sk} \rangle = \sum_k e^{sk} p(k) = 1 + s\langle k \rangle + \frac{s^2}{2} \langle k^2 \rangle + \dots$$

$$(\text{or, equivalently: } \langle e^{sx} \rangle = \int dx e^{sx} p(x))$$

$$\langle k \rangle = \frac{d}{ds} \langle e^{sk} \rangle \Big|_{s=0}, \quad \langle k^2 \rangle = \frac{d^2}{ds^2} \langle e^{sk} \rangle \Big|_{s=0}, \quad \langle k^n \rangle = \dots$$

$$\langle k \rangle_{\text{binomial}} = \frac{d}{ds} \sum_k \binom{n}{k} p^k q^{n-k} e^{sk} \Big|_{s=0} = \frac{d}{ds} \sum_k \binom{n}{k} (pe^s)^k q^{n-k} \Big|_{s=0} =$$

$$= \frac{d}{ds} (pe^s + q)^n \Big|_{s=0} = np (pe^s + q)^{n-1} e^s \Big|_{s=0} = np$$

$$\langle k^2 \rangle = \frac{d^2}{ds^2} (pe^s + q)^n \Big|_{s=0} = np [(n-1)(pe^s + q)^{n-2} pe^{2s} + (pe^s + q)^{n-1} e^s] \Big|_{s=0} =$$

$$= np[(n-1)p + 1] = (np)^2 - np^2 + np = \langle k \rangle^2 - np(p-1) = \langle k \rangle^2 + npq$$

$\text{Var}(k) = npq$  as already found at page 12. For Poisson:

$$\langle k \rangle = \frac{d}{ds} \sum \frac{(at)^k}{k!} e^{-at} e^{sk} \Big|_{s=0} = \frac{d}{ds} \sum \frac{(at e^s)^k}{k!} e^{-at} \Big|_{s=0} = \frac{d}{ds} at(e^s - 1) \Big|_{s=0}$$

$$= e^{at(e^s - 1)} at e^s \Big|_{s=0} = at$$

$$\langle k^2 \rangle = at \frac{d}{ds} (e^{at(e^s - 1)} e^s) \Big|_{s=0} = at \left( at e^{at(e^s - 1)} e^{2s} + e^{at(e^s - 1)} e^s \right) \Big|_{s=0}$$

$$= at(at + 1) = (at)^2 + at = \langle k \rangle^2 + \langle k \rangle, \quad \text{Var}(k) = \langle k \rangle$$

## THE NORMAL DISTRIBUTION

Let's derive another approx. of  $P_B(k)$  in the limit of large  $n$  and large  $\langle k \rangle = np$ , where  $n$  can be considered a continuous variable (Poisson was obtained for  $np \approx 1$ ).

We follow Reif 1.5 (Feller and Arfken-Weber follow a more complicated path...), simply expanding  $\log P_B(k)$  up to second order around  $k = \langle k \rangle$ , with  $x = k - \langle k \rangle$ :

$$\log P_B(k) \approx \log P_B(\langle k \rangle) + \frac{d \log P_B}{dk} \Big|_{\langle k \rangle} x + \frac{1}{2} \frac{d^2 \log P_B}{dk^2} \Big|_{\langle k \rangle} x^2$$

$$\log P_B(k) = \log n! - \log k! - \log(n-k)! + k \log p + (n-k) \log q$$

$$\text{for large } n \quad \frac{d}{dn} \log(n!) \approx \frac{\log(n+1)! - \log n!}{1} = \log(n+1) \approx \log n$$

(since 1 is a small increment, producing a relatively small variation of  $n!$  for large  $n$ )

$$\frac{d}{dk} \log P_B(k) \approx -\log k + \log(n-k) + \log p - \log q$$

$$\text{we set to zero to find maximum: } \log \frac{n-k}{k} = \log \frac{q}{p}, \\ \frac{n}{k} - 1 = \frac{q}{p}, \quad \frac{n}{k} = \frac{q}{p} + 1 = \frac{1}{p}, \quad k = np = \langle k \rangle$$

So peak is equal to average. First derivative is zero at the maximum, only 2<sup>nd</sup> derivative survives:

$$\frac{d^2}{dk^2} \log P_B(k) \Big|_{np} \approx \left( -\frac{1}{k} - \frac{1}{n-k} \right)_{np} = -\frac{1}{np} - \frac{1}{n-np} = -\frac{1}{n} \left( \frac{1}{p} + \frac{1}{q} \right) \\ = -\frac{1}{npq} = -\frac{1}{\text{Var}(k)} \equiv -\frac{1}{\sigma^2} < 0 \quad (\text{since it is at maximum})$$

We can stop the expansion to 2<sup>nd</sup> order if  $x \ll npq$  (because the 3<sup>rd</sup> order term is  $\propto (npq)^{-2}$ , so it is negligible compared to the 2<sup>nd</sup> order one if  $x/npq \ll 1$  ... see Reif 1.5):

$$\text{we obtain } \log P_B(k = \langle k \rangle + x) \approx C - \frac{1}{2} \frac{x^2}{\sigma^2} = C - \frac{1}{2} \frac{(k - \langle k \rangle)^2}{\sigma^2}$$

(21)

which gives the normal (Gaussian) distrib. (De Moivre-Laplace Th.)

$$p_G(x) = C e^{-\frac{1}{2}(\kappa - \langle \kappa \rangle)^2 / \sigma^2} \quad \langle \kappa \rangle = np, \quad \sigma^2 = npq$$

error w.r.t. binomial distrib. is small if  $npq$  is large and if we don't go too much in the tails ( $\kappa - \langle \kappa \rangle \ll npq$ ), with  $np \gg 1$  (Gaussian is symmetric, contrary to binomial and Poisson, so it works if we stay far from  $\kappa \approx 0$ ), whereas for  $np \approx 1$  we can use safely Poisson. If both  $np \gg 1$  and  $npq \gg 1$  we can use both Poisson and Gaussian: for example for  $n=10^8$ ,  $p=10^{-6}$ ,  $np=100$ ,  $npq \approx np$ . Binomial is the exact result, but impractical for large  $n$  due to factorials, whereas Poisson and Gaussian are handy. (show example counting random points falling in subinterval of  $[0,1]$ : binomial exact, Poisson and Gaussian can be good).

Normalization constant  $C$ :  $\int dx p_G(x) = 1$ , we use trick:

$$\left( \int_{-\infty}^{\infty} dx p_G(x) \right)^2 = \int_{-\infty}^{\infty} dx \int_{-\infty}^{\infty} dy p_G(x) p_G(y) = C^2 \int_0^{2\pi} r d\theta \int_0^{\infty} dr e^{-\frac{1}{2}r^2/\sigma^2}$$

$$= 2\pi C^2 \int_0^{\infty} dr r e^{-\frac{1}{2}r^2/\sigma^2} \quad \text{and since } \frac{d}{dr} e^{-\frac{1}{2}r^2/\sigma^2} = -\frac{r}{\sigma^2} e^{-\frac{1}{2}r^2/\sigma^2}.$$

$$2\pi C^2 (-\sigma^2) \left( e^{-\frac{1}{2}\sigma^2} \right)_0^{\infty} = 2\pi C^2 \sigma^2 = 1 \Rightarrow C = \frac{1}{\sqrt{2\pi}\sigma}$$

$$p_G(x) = \frac{1}{\sqrt{2\pi}\sigma} e^{-\frac{1}{2}(x-\langle x \rangle)^2/\sigma^2}$$

It is remarkable how a few famous prob. distrib. dominate prob. theory, with infinite applications. We'll see some reasons why Gaussian, in particular, is ubiquitous. [Reft pag. 18: we Taylor expand  $\log p_G$  instead of  $p_G$ , because when  $n\delta^n$  expansion does not converge!]

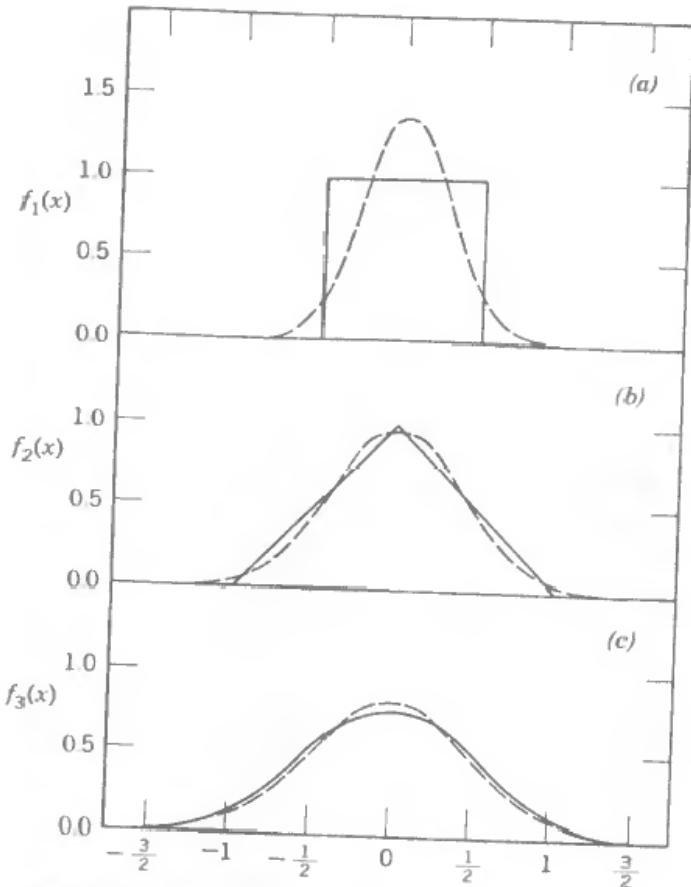


FIGURE 21.1

Convergence of probability density to the Gaussian form. The probability density for systems composed of one, two and three elements, each with the probability density shown in Figure 21.1a. In each case the Gaussian with the same standard deviation is plotted. In accordance with the central limit theorem the probability density becomes Gaussian for large  $\tilde{N}$ .

# TD5

**Ex. 1.1:** This is the most obvious application of the Poisson law (it should be given immediately in books!): we put  $N$  random points in a segment of length  $L$  (time or space, any dimensionality, it does not matter), with uniform density, and we ask how many points fall in a subinterval that is small enough to contain, on average, a few points (let's say, of size  $\sim L/N$ ). The answer is Poisson law. Nice features: the average density is the only parameter, and the shape of the interval does not matter (it can be a collection of segments in 1D, any shape in 2D or 3D...). Think to rain drops falling on a surface.

Poisson law is at the core of statistical analyses in simulations, e.g., number of configurations from equilibrium MD, falling in an interval of an order parameter, are assumed to be Poisson distributed (histogram analysis...). Of course one can check (Kolmogorov-Smirnov etc.) that an observed distribution is similar to Poisson or not. If not, one can try to understand what is the origin of deviations (correlations?).

MEAN FIRST PASSAGE TIME OF POISSON PROCESS

$$mfpt = \int_0^\infty dt t p(t) \quad \text{where } p \text{ is prob. dens. function}$$

to observe first passage in  $[t, t+dt]$

$$p(t) dt = p_0(t) p_1(dt) \quad \text{where } p_k(t) = (t/\tau)^k \frac{e^{-t/\tau}}{k!}$$

zero jumps      one jump      (Poisson prob.)

until  $t$       in  $dt$       (product since bins intervals are  
indep. in Poisson pr.)

$$= e^{-t/\tau} \cdot \frac{dt}{\tau} e^{-dt/\tau} \approx e^{-t/\tau} \frac{dt}{\tau}$$

normalization:  $\int_0^\infty p(t) dt = \frac{1}{\tau} \int_0^\infty e^{-t/\tau} dt = [-e^{-x}]_0^\infty = 1$

$$mfpt = \int_0^\infty t p(t) dt = \int_0^\infty \frac{t}{\tau} e^{-t/\tau} dt = \tau \int_0^\infty x e^{-x} dx$$

$$\left( = [-x e^{-x}]_0^\infty - \int_0^\infty (-e^{-x}) dx = 0 + \int_0^\infty e^{-x} dx = 1 \right) \tau = \tau$$

where we implicitly assumed that, for small  $dt$ ,  $dt/\tau \ll 1$ ,  $p_{k>1}(dt) \ll p_1(dt)$  so in practice only the first event can be observed and not two events in a small  $dt$ .

Let's compute fluctuations of fpt:

$$\langle fpt^2 \rangle = \int_0^\infty t^2 p(t) dt = \int_0^\infty \frac{t^2}{\tau} e^{-t/\tau} dt = \tau^2 \int_0^\infty x^2 e^{-x} dx = 2\tau^2$$

(note that  $\int_0^\infty x^n e^{-ax} dx = n! / a^{n+1}$  for  $n=0,1,2,\dots$ ,  $\text{Re}(a) > 0$ )

$$\sigma_{fpt} = \sqrt{\langle fpt^2 \rangle - \langle fpt \rangle^2} = \sqrt{2\tau^2 - \tau^2} = \tau$$

so, in Poisson process,  $\langle k \rangle = \langle k^2 \rangle = t/\tau$ , while first passage time has mean = std deviation =  $\tau$ .

Note that diff. eq. can be obtained from Fick's law.  $\vec{J} = -D \vec{\nabla} N$   
as continuity eq:  $\frac{\partial N}{\partial t} + \vec{\nabla} \cdot \vec{J} = 0$ , and law  $\langle x^2 \rangle = 2Dt$

can be found from diff. eq. multiplying by  $x^2$  and integrating:

$$\int_{-\infty}^{\infty} dx x^2 \frac{\partial N}{\partial t} = D \int_{-\infty}^{\infty} dx x^2 \frac{\partial^2 N}{\partial x^2} \quad (\text{Reif 12.5})$$

$$\frac{\partial}{\partial t} \int_{-\infty}^{\infty} dx x^2 N = \frac{\partial}{\partial t} \langle x^2 \rangle N_{\text{tot}}$$

$$\int_{-\infty}^{\infty} dx x^2 \frac{\partial^2 N}{\partial x^2} = \left[ x^2 \frac{\partial N}{\partial x} \right]_{-\infty}^{\infty} - 2 \int_{-\infty}^{\infty} dx x \frac{\partial N}{\partial x} = 0 - 2 \left[ xN \right]_{-\infty}^{\infty} + 2 \int_{-\infty}^{\infty} dx N = 2N_{\text{tot}}$$

(because for  $x \rightarrow \pm\infty$ ,  $\frac{\partial N}{\partial x} \rightarrow 0$  and  $N \rightarrow 0$ ) thus

$$\frac{\partial}{\partial t} \langle x^2 \rangle = 2D, \quad \langle x^2 \rangle = 2Dt + c \quad (c=0 \text{ since } \langle x^2 \rangle = 0 \text{ at } t=0)$$

Laplacian is hallmark of irreversibility!

Note: in 1D, 2D random walk has  $P=1$  to return to origin (thus,  $\infty$  times),  
in 3D  $P \approx 0.35$ , so it may never return (Filler ch XIV).

③

XXX Find a nice, simple way to explain why Laplacian introduces irreversibility (Fokker-Planck eq.), as compared to first derivatives (Liouville eq.), that instead give time-reversibility without second principle; coarse-graining leads to Laplacian and, thus, to irreversibility and second principle (see, e.g., Mackay Rev. Mod. Phys. 1989, or Tuckerman, Penrose...).

**Ex. 2.2:** We can notice that the variance of the Gaussian is  $2Dt$  as in Einstein's law (the mean is zero: no drift forces like in sedimentation...).

The distribution at  $t = 0$  is a Dirac delta: actually one way to define the Dirac delta is the limit for the variance going to zero of a normalized Gaussian...

In 3D, one has to be careful about normalization in the prefactor, and about the proper form of the exponent, since it is easy to make mistakes: to avoid confusion, think about statistical independence of the three directions

$$\rho_{3D}(\mathbf{r}, t) = \rho(x, t)\rho(y, t)\rho(z, t) = \frac{1}{(4\pi Dt)^{3/2}} e^{-r^2/4Dt}$$

which gives correct normalization:

$$\int d^3r \rho_{3D}(\mathbf{r}, t) \equiv \int dx \rho(x, t) \int dy \rho(y, t) \int dz \rho(z, t) = 1$$

Note: continuous prob. distributions are insidious, source of many errors in exams, since changes of variables must be well understood, and it is better to write  $\rho_{3D}(\mathbf{r}, t)$  instead of  $\rho_{3D}(r, t)$ , even though the functional form depends explicitly only on the scalar  $r$ , because the vector notation reminds us that we need to integrate over 3D space  $dx dy dz$  and not over 1D  $dr$ , for instance. Stress this point, we'll see troubles with Maxwell-Boltzmann distribution in later TD, when passing from  $\mathbf{v}$  to scalar  $v$  as argument of the distribution.

Diffusion can be seen as continuous limit of random walk (see the following exercise), where we sum many small random displacements, each one characterised by a finite-value distribution (no matter the shape), thus an excellent application of the central limit theorem.

For long time, particles spread out evenly in the available space (stationary distribution at equilibrium, time-independent): if it is a finite box, we get uniform density. By contrast, if we add gravity along one direction (sedimentation) we would get an exponentially decaying stationary distribution, according to the canonical (Boltzmann) distribution:

$$\rho(z, t) = C e^{-mgz/kT}$$

Clearly, the dynamics as represented by the diffusion eq. is irreversible, despite the time-reversibility of Hamilton's eq.: the apparent paradox is solved noting that the diffusion eq. is just an approximated model, coarse-grained, while Hamilton's eq. are exact. In other words, irreversibility is only apparent, in reality there is a finite (but very small) probability to observe the particles go back close to the initial configuration. We just don't usually see it within our lifetime (or the one of the universe), if we have many particles, but if they are a few tens it could be seen. See the nice discussion based on Poincaré recurrence at the end of Zwanzig's book "non-equilibrium statistical mechanics".

to connect random walk model with diffusion equation, consider  $N_{tot} \gg 1$  walkers, discretize position  $x_k = k\Delta x = kl$ , and split total frequency into jumps to the left and to the right (as probabilities add up!):

$$\nu = \nu_- + \nu_+ = 2\nu_\pm$$

if  $N(x_k, t)$  is the number of walkers at position  $x_k$  at time  $t$ , at time  $t + \Delta t$  the number decreases due to walkers jumping from  $x_k$  to  $x_{k\pm 1}$  and it increases due to walkers jumping from  $x_{k\pm 1}$  to  $x_k$ :

$$N(x_k, t + \Delta t) - N(x_k, t) = -\nu_- \Delta t N(x_k, t) - \nu_+ \Delta t N(x_k, t) + \nu_+ \Delta t N(x_{k-1}, t) + \nu_- \Delta t N(x_{k+1}, t)$$

$$\frac{N(x_k, t + \Delta t) - N(x_k, t)}{\Delta t} = \nu_\pm [N(x_{k-1}, t) - 2N(x_k, t) + N(x_{k+1}, t)]$$

for large  $N_{tot}$ , small  $l$  and small  $\Delta t$  finite differences  $\rightarrow$  derivatives:

$$\frac{\partial N}{\partial t} = \nu_\pm l^2 \frac{\partial^2 N}{\partial x^2} = D \frac{\partial^2 N}{\partial x^2}$$

a more general case:

- replace the position  $x$  with any generalized coordinate (or order parameter)  $q$
- different regions of space have different equilibrium probabilities  $\rho(q, t \rightarrow \infty) \equiv \rho_{eq}(q) = e^{-F(q)/kT}$  ( $F$  = free energy landscape)
- $D(q)$  is a function of the position

$$\frac{\partial \rho(q, t)}{\partial t} = \frac{\partial}{\partial q} \left[ D(q) e^{-F(q)/kT} \frac{\partial}{\partial q} \left( e^{F(q)/kT} \rho(q, t) \right) \right]$$

this is the Fokker-Planck eq. describing diffusion on a landscape (e.g., crystal nucleation, protein folding...), described later in this course

for constant  $D, F$  you recover the simple diffusion eq.

# TD6

## Ex. 1.1 ideal gas

### EXAMPLE: IDEAL GAS

In general we have  $H = \sum_1^N \frac{\vec{p}_i^2}{2m} + V(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N)$  and we now need distrib. In continuous phase space, however, in line with microcanonical discussion, we divide into minimal volumes  $\hbar^{3N}$  due to compatibility with QM, leading to adimensional  $Z$ , and we divide by  $N!$  to avoid Gibbs paradox:

$$P(\vec{q}, \vec{p}) = \frac{e^{-\beta H(\vec{q}, \vec{p})}}{\int d\vec{q} d\vec{p} e^{-\beta H}}, \quad Z = \frac{1}{\hbar^{3N} N!} \int d\vec{q} d\vec{p} e^{-\beta H(\vec{q}, \vec{p})}$$

$$Z = \frac{1}{N! \hbar^{3N}} \int d^{3N} \vec{r} e^{-\beta V(\vec{r})} \int d^{3N} \vec{p} e^{-\beta \sum \vec{p}_i^2 / 2m}$$

The first integral can be very difficult, the second is easy.

In a ideal gas we assume  $V \approx 0$  (high dilution), so we get

## Ex. 1.2 paramagnetism

$$\begin{aligned}
Z &= \frac{z^N}{N!}, \quad z = \frac{V}{h^3} \int e^{-(\beta/2m)\vec{p}^2} d^3\vec{p} = \\
&= \frac{V}{h^3} \int_{-\infty}^{\infty} dp_x e^{-(\beta/2m)p_x^2} \int_{-\infty}^{\infty} dp_y e^{-(\beta/2m)p_y^2} \int_{-\infty}^{\infty} dp_z e^{-(\beta/2m)p_z^2} \\
&= \frac{V}{h^3} \left( \sqrt{\frac{\pi}{\beta/2m}} \right)^3 \quad (\text{since } \int_{-\infty}^{\infty} dx e^{-\alpha x^2} = \sqrt{\frac{\pi}{\alpha}}) \\
&= V \left( \frac{2\pi m}{h^2 \beta} \right)^{3/2}, \quad Z = \frac{V^N}{N!} \left( \frac{2\pi m}{h^2 \beta} \right)^{3N/2} = \frac{1}{N!} \frac{V^N}{\lambda^{3N}}, \quad \lambda = \sqrt{\frac{\beta h^2}{2\pi m}}
\end{aligned}$$

$$\log Z = N \log V - \log N! + \frac{3N}{2} \log \left( \frac{2\pi m}{h^2 \beta} \right) \quad \text{"thermal wavelength" \uparrow} \\
\approx N \log V - N \log N + N + \frac{3N}{2} \log \left( \frac{2\pi m}{h^2 \beta} \right) \quad (\text{Tuckerman 11.3:})$$

$\lambda = \sqrt{\frac{\beta h^2}{2\pi m}}$  both cl. and quantum ideal gas of distinguishable particles have  $Z = V^N / \lambda^{3N}$

which has similar structure w.r.t.  $\log Z$  obtained in NVE ensemble (pag. 55). To extract useful information we need to make some analysis of partition function properties.

$$\begin{aligned}
F &= -kT \log Z = -NkT \left[ \log \frac{V}{N} + \frac{3}{2} \log \left( \frac{2\pi m kT}{h^2} \right) + \frac{5}{2} \right] \\
(*) \quad S &= -\frac{\partial F}{\partial T} = Nk \left[ \log \frac{V}{N} + 1 + \frac{3}{2} \log \left( \frac{2\pi m kT}{h^2} \right) + \frac{3}{2} \right] \\
&= Nk \left[ \log \frac{V}{N} + \frac{3}{2} \log \left( \frac{2\pi m kT}{h^2} \right) + \frac{5}{2} \right]
\end{aligned}$$

$$\text{but } E = \frac{3}{2} NkT \Rightarrow kT = \frac{2E}{3N},$$

$$S = Nk \left[ \log \frac{V}{N} + \frac{3}{2} \log \left( \frac{4\pi m E}{3N h^2} \right) + \frac{5}{2} \right]$$

Sackur-Tetradec! équivalence entre ens...

### EXAMPLE: PARAMAGNETISM (Ref. 6.3)

Consider  $N$  magnetic atoms in a volume  $V$ , interacting very weakly with each other and with the other degrees of freedom (e.g. other non-magnetic atoms), and assume that each magnetic atom can be distinguished (e.g. they are impurity atoms in a crystal, at fixed lattice positions): in these conditions we can consider each atom as a small system in contact with a heat reservoir (i.e., the rest of the system). Note that the 2 derivations of the canonical ensemble do not require subsystem 1 to be large, so we can apply canonical distrib.

We consider the system immersed in external magnetic field  $\vec{H}$ , so that each magnetic atom has energy  $-\mu \vec{\mu} \cdot \vec{H}$ , and we assume  $\text{spin} = \pm 1/2$  in the direction of  $\vec{H}$ , hence energies are  $-\mu H$  (parallel spin) or  $+\mu H$  (antiparallel spin)

$$P_+ = \frac{1}{Z} e^{-\beta E_+} = \frac{1}{Z} e^{\beta \mu H}, \quad P_- = \frac{1}{Z} e^{-\beta \mu H}, \quad Z = e^{\beta \mu H} + e^{-\beta \mu H}.$$

$P_+ > P_-$ , distribution in states + and - depends on  $\mu H / kT$ :

$$\begin{aligned} \langle \mu_H \rangle &= \frac{1}{Z} \sum_a P_a \mu_a = \frac{1}{Z} (P_+ \mu - P_- \mu) = \mu \frac{e^{\beta \mu H} - e^{-\beta \mu H}}{e^{\beta \mu H} + e^{-\beta \mu H}} = \\ &= \mu \tanh\left(\frac{\mu H}{kT}\right) \end{aligned}$$

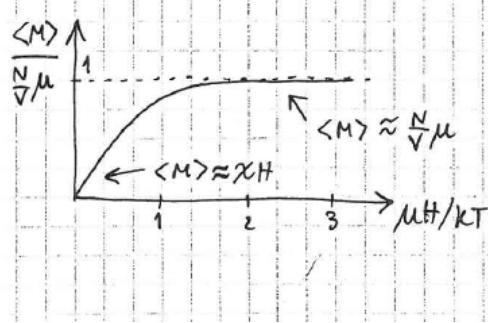
(75)

calling  $\mu H / kT = y$ , for  $y \ll 1$   $\tanh y = \frac{(1+y+\dots)-(1-y+\dots)}{(1+y+\dots)+(1-y+\dots)} \approx y$   
so for  $\mu H \ll kT$   $\langle \mu_H \rangle \approx \mu^2 H / kT$

for  $y \gg 1$   $e^y \gg e^{-y}$ ,  $\tanh y = \frac{e^y - e^{-y}}{e^y + e^{-y}} \approx \frac{e^y}{e^y} = 1$

so for  $\mu H \gg kT$   $\langle \mu_H \rangle \approx \mu$

The magnetization is  $\langle M \rangle = \frac{N}{V} \langle \mu_B \rangle$  : at high T it is linear in the field H  $\langle M \rangle \approx \chi H$  with  $\chi = \frac{N \mu^2}{V kT}$  (susceptibility)  $\approx T^{-1}$  (Curie's law), whereas for low T  $\langle M \rangle \rightarrow \frac{N}{V} \mu$  is the maximum value (saturation), indep of H :



### Ex. 1.3 entropy in absence or presence of correlations

#### SOME PROPERTIES OF GIBBS ENTROPY (Ref. ex. 6.13-15)

As shown above,  $S = -k \sum p_\alpha \log p_\alpha$  can be obtained from  $S = k \log \Omega$  and is valid in generic ensembles, it's more handy than Boltzmann formula since prob. is easier to write than  $\Omega$ , in general. We can take Gibbs formula as basis to connect with 2<sup>nd</sup> principle and with thermodynamics.

A basic property of entropy is additivity (extensivity): given 2 statistically independent subsystems, with no- or weak interaction between them,

$$S_A = -k \sum p_\alpha^A \log p_\alpha^A, \quad S_B = -k \sum p_\alpha^B \log p_\alpha^B$$

$$P_{\alpha\alpha'}^{AB} = P_\alpha^A P_{\alpha'}^B, \quad S_{AB} = -k \sum_{\alpha \alpha'} P_{\alpha\alpha'}^{AB} \log P_{\alpha\alpha'}^{AB} = \\ = -k \sum_{\alpha \alpha'} P_\alpha^A P_{\alpha'}^B [\log P_\alpha^A + \log P_{\alpha'}^B] = S_A + S_B$$

Note that if interaction between A and B is negligible

$$P_{\alpha\alpha'}^{AB} = \frac{e^{-\beta E_\alpha^A} e^{-\beta E_{\alpha'}^B}}{\sum_{\alpha \alpha'} e^{-\beta E_\alpha^A} e^{-\beta E_{\alpha'}^B}} = \frac{e^{-\beta E_\alpha^A}}{Z_A} \frac{e^{-\beta E_{\alpha'}^B}}{Z_B} = P_\alpha^A P_\beta^B$$

If the interaction is not negligible, simplifying notation

$$P_{\alpha\gamma} \neq P_\alpha^A P_\gamma^B, \quad P_\alpha^A = \sum_\gamma P_{\alpha\gamma}, \quad P_\gamma^B = \sum_\alpha P_{\alpha\gamma},$$

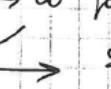
$$\sum_\alpha \sum_\gamma P_{\alpha\gamma} = \sum_\alpha P_\alpha^A = \sum_\gamma P_\gamma^B = 1$$

$$S - (S_A + S_B) = -k \sum_{\alpha\gamma} P_{\alpha\gamma} \log P_{\alpha\gamma} + k \left[ \sum_\alpha P_\alpha^A \log P_\alpha^A + \sum_\gamma P_\gamma^B \log P_\gamma^B \right]$$

$$= -k \sum_{\alpha\gamma} \left[ P_{\alpha\gamma} (\log P_{\alpha\gamma} - \log P_\alpha^A - \log P_\gamma^B) \right]$$

$$= k \sum_{\alpha\gamma} P_{\alpha\gamma} \log \left( \frac{P_\alpha^A P_\gamma^B}{P_{\alpha\gamma}} \right)$$

Now, one can show that  $\log x \leq x-1$  (since  $f(x) = x - \log x$

is characterized by  $f \rightarrow \infty$  for  $x \rightarrow 0$  and  $x \rightarrow \infty$ ,  $df/dx = 1 - 1/x = 0$  for  $x=1$ :  so  $f \geq 1$ , or  $x-1 \geq \log x$ ) so

$$k \sum_{\alpha\gamma} P_{\alpha\gamma} \log \left( \frac{P_\alpha^A P_\gamma^B}{P_{\alpha\gamma}} \right) \leq k \sum_{\alpha\gamma} \left( P_\alpha^A P_\gamma^B - P_{\alpha\gamma} \right) = 0$$

$$S \leq S_A + S_B \quad (\text{equal sign if } P_{\alpha\gamma} = P_\alpha^A P_\gamma^B)$$

Careful: interpretation of  $S$  (with correlations)  $\leq S$  (without correlation) can be tricky, since adding interactions introduce correlations, but then one might think that removing wall between two systems should reduce entropy, that is absurd. I think the latter experiment does not correspond to the calculations above, because the argument was: we keep the same marginal probabilities and we pretend we can compute  $S_A + S_B$  as if  $A$  and  $B$  were independent, but this is false, so it does not correspond to the experiment where we remove the wall. In the latter experiment, the marginal probabilities would change!

## Ex. 2.1

(Taken from Ngo & Ngo "Physique statistique", 13.6; Derrida "Fluctuations et grandes deviations autour du Second Principe", 3.2)

$$\frac{dp_i}{dt} = \sum_{j=1}^n (K_{ij} p_j - K_{ji} p_i)$$

where  $K_{ij} \equiv K_{i \leftarrow j}$ ,  $K_{ji} \equiv K_{j \leftarrow i}$ . We know that, at equilibrium  $dp_i/dt = 0 \forall i$ , thus  $K_{ij} p_j = K_{ji} p_i$ . We are told that macrostates at equilibrium ( $t \rightarrow \infty$ ) are equiprobable, so  $K_{ij} = K_{ji}$ . (note that this would be also the case if the macrostates were actually microstates of an almost isolated quantum system, hence with similar energy within  $\delta E$  (Heisenberg's principle...), assuming a master equation to hold due to small external perturbations, as in Ngo's argument).

$$\frac{dS}{dt} = -k \sum_i \left[ \frac{dp_i}{dt} \log(p_i) + \frac{dp_i}{dt} \right]$$

where  $\sum_i dp_i/dt = d(\sum_i p_i)/dt = d1/dt = 0$ , so

$$\frac{dS}{dt} = -k \sum_i \frac{dp_i}{dt} \log(p_i) = -k \sum_i \sum_j (K_{ij} p_j - K_{ji} p_i) \log(p_i) = k \sum_i \sum_j K_{ij} (p_i - p_j) \log(p_i)$$

where we used  $K_{ij} = K_{ji}$ . Now, we realize that we get the same equation by exchanging  $i$  with  $j$  (they are just dummy indices), and we add the two resulting equations:

$$2 \frac{dS}{dt} = k \sum_i \sum_j K_{ij} (p_i - p_j) [\log(p_i) - \log(p_j)]$$

but the logarithm is a monotonic function, so  $(p_i - p_j)$  has the same sign of  $[\log(p_i) - \log(p_j)]$ , therefore  $dS/dt \geq 0$ .

## Ex. 2.2

From Tuckerman (solution manual), ex. 2.6, where  $f \equiv \rho$  and  $\eta$  is the phase-space velocity:

- 2.6. a. The time derivative of  $S(t)$  is determined by the Liouville equation for  $f(x, t)$ .

We can see this by computing the time derivative of  $S(t)$ , taking care of how we interpret the time derivative outside and under the integral sign. That is, if we look at

$$\frac{dS}{dt} = -k \frac{d}{dt} \int dx f(x, t) \ln f(x, t)$$

the total time derivative outside the integral sign acts on the explicit time dependence only. Thus, if we bring it under the integral sign, we must do so as a partial derivative:

$$\begin{aligned} \frac{dS}{dt} &= -k \int dx \left[ \frac{\partial f}{\partial t} + \ln f \frac{\partial f}{\partial t} \right] \\ &= -k \int dx \frac{\partial f}{\partial t} [1 + \ln f] \end{aligned}$$

Now because  $f(x, t)$  satisfies the Liouville equation, which as a partial differential equation is

$$\frac{\partial}{\partial t} f(x, t) = -\eta(x, t) \cdot \nabla f(x, t)$$

we can rewrite  $dS/dt$  as

$$\frac{dS}{dt} = k \int dx [1 + \ln f(x, t)] \eta(x, t) \cdot \nabla f(x, t)$$

We now integrate by parts, recognizing that  $f(x, t)$  vanishes at the boundary of phase space:

$$\begin{aligned} \frac{dS}{dt} &= -k \int dx \nabla [1 + \ln f(x, t)] \cdot \eta(x, t) f(x, t) \\ &= -k \int dx \nabla f(x, t) \cdot \eta(x, t) \end{aligned}$$

Integrating once again by parts gives

$$\frac{dS}{dt} = k \int dx f(x, t) \nabla \cdot \eta(x, t) = 0$$

since we assume the equations of motion to be incompressible.

# TD7

$$(1.1) \quad p(v_x) = \int d\Gamma e^{-\beta H} / \int d\Gamma e^{-\beta H}$$

TD7

$$H = \frac{mv_x^2}{2} + \dots \Rightarrow p(v_x) = \frac{e^{-\beta m v_x^2/2}}{C}$$

$$C = \int_{-\infty}^{\infty} dv_x e^{-\beta m v_x^2/2} = \sqrt{2\pi\sigma^2} = \sqrt{2\pi kT/m}$$

$$(1.2) \quad \langle v_x \rangle = \int dv_x v_x p(v_x) = 0 \quad (\text{symétrie...})$$

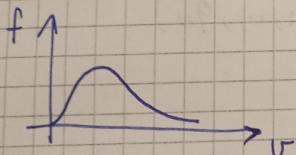
$$\sigma^2 \equiv \langle v_x^2 \rangle = kT/m, \quad \frac{m \langle v_x^2 \rangle}{2} = \frac{kT}{2}$$

valeur plus probable  $\approx \max \text{ de } p(v_x) \equiv 0$

$$(1.3) \quad f(v) = ? \quad g(\vec{v}) = \sqrt{\frac{\rho m}{2\pi}}^3 e^{-\beta m \vec{v}^2/2} \quad (\vec{v}^2 \equiv v^2)$$

$$g(\vec{v}) d^3v = g(v) 4\pi v^2 dv = f(v) dv$$

$$\Rightarrow f(v) = \left( \frac{\rho m}{2\pi} \right)^{3/2} 4\pi v^2 e^{-\beta m v^2/2} \quad \leftarrow \text{Maxwell-Boltzmann}$$



$$(1.4) \quad \langle v^2 \rangle = \langle v_x^2 \rangle + \langle v_y^2 \rangle + \langle v_z^2 \rangle = 3 \langle v_x^2 \rangle = 3kT/m$$

$$\Rightarrow T = m \langle v^2 \rangle / 3k$$

equipartition ici: chaque d.o.f. de vitesse à  $\frac{kT}{2}$

$$(1.5) \quad p(\vec{q}_1, \dots, \vec{q}_N, \vec{p}_1, \dots, \vec{p}_N) = e^{-\beta H} / \int d^{3N}q \int d^{3N}p e^{-\beta H}$$

$$= \prod_{i=1}^N \tilde{p}(\vec{p}_i) \cdot e^{-\beta U(\vec{q}_1, \dots, \vec{q}_N)} / \int d^3q e^{-\beta U}$$

$$(2.1) \quad \tilde{p}(\vec{p}_i) = e^{-\beta p_i^2/2m} / D, \quad D = \sqrt{2\pi\sigma^2} = \sqrt{2\pi m kT}$$

$$\begin{aligned}
 \textcircled{2.2} \quad & \tilde{\rho}(\vec{p}) d^3 p = f(E) dE \\
 & \text{commes} \quad \text{incommu} \\
 & d^3 p = 4\pi p^2 dp, \quad p^2 = 2mE, \quad 2pd\vec{p} = 2mdE \\
 & d^3 p = 2\pi p \cdot 2mdE = 4\pi m \sqrt{2mE} dE \\
 & \tilde{\rho}(\vec{p}) = (2\pi m kT)^{-3/2} e^{-\beta p^2/2m} = (2\pi m kT)^{-3/2} e^{-\beta E} \\
 & \tilde{\rho}(\vec{p}) d^3 p = (2\pi m kT)^{-3/2} e^{-\beta E} \cdot 4\pi m \sqrt{2mE} dE \equiv f(E) dE \\
 & f(E) = \frac{2}{\sqrt{\pi}} (kT)^{-3/2} \sqrt{E} dE
 \end{aligned}$$

$$\textcircled{3.1} \quad Z = \frac{1}{h^{3N} N!} \int d^3 q \int d^3 p e^{-\beta H} = \frac{1}{h^{3N} N!} \int d^3 q e^{-\beta U} \int d^3 p e^{-\beta K}$$

$$Z_{\text{kin}} = \left[ \int d\vec{p} e^{-\beta p^2/2m} \right]^{3N} = \sqrt{2\pi\sigma^2}^{3N} = (2\pi m kT)^{3N/2}$$

$$Z = \underbrace{(2\pi m kT/h^2)^{3N/2}}_{1^{-3N}} \frac{1}{N!} \int d^3 q e^{-\beta U(\vec{q}_1, \dots, \vec{q}_N)}$$

$1^{-3N}$  ← longueur d'onde Hermique

$$\textcircled{3.2} \quad \langle A(\vec{q}_1, \dots, \vec{q}_N) \rangle = \int d^3 q A e^{-\beta U} / \int d^3 q e^{-\beta U}$$

$$\langle B(\vec{p}_1, \dots, \vec{p}_N) \rangle = \int d^3 p B e^{-\beta K} / \int d^3 p e^{-\beta K}$$

## EQUIPARTITION THEOREM

Consider an Hamiltonian where a degree of freedom  $q_i$  or  $p_i$  contributes a quadratic term :  $H = \alpha q_i^2 + H'(\text{other d.o.f.}) = H_i + H'$  (e.g.  $p_i^2/2m, \frac{1}{2}mw^2q_i^2\cdots$ )

$$\begin{aligned}\langle E_i \rangle &= \frac{\int d\vec{q} d\vec{p} H_i e^{-\beta H}}{\int d\vec{q} d\vec{p} e^{-\beta H}} = \frac{\int dq_i H_i e^{-\beta H_i}}{\int dq_i e^{-\beta H_i}} \frac{\int d\vec{q}' d\vec{p}' e^{-\beta H'}}{\int d\vec{q}' d\vec{p}' e^{-\beta H'}} = \\ &= -\frac{\partial}{\partial \beta} \frac{\int dq_i e^{-\beta H_i}}{\int dq_i e^{-\beta H_i}} = -\frac{\partial}{\partial \beta} \log \left[ \int dq_i e^{-\beta H_i} \right] = \\ &= -\frac{\partial}{\partial \beta} \log \left[ \int dq_i e^{-\beta \alpha q_i^2} \right] = -\frac{\partial}{\partial \beta} \log \sqrt{\frac{\pi}{\beta \alpha}} = \\ &= -\frac{\partial}{\partial \beta} \left[ \frac{1}{2} \log \frac{\pi}{\alpha} - \frac{1}{2} \log \beta \right] = \frac{1}{2\beta} = \frac{kT}{2}.\end{aligned}$$

So each degree of freedom contributing a quadratic term to the  $H$  has average energy  $kT/2$ . We saw that in ideal gas  $H = \sum_1^N \vec{p}_i^2/2m \Rightarrow \langle \vec{p}_i^2/2m \rangle = 3kT/2, \langle E \rangle = \frac{3}{2} N kT$ , for  $N$  1-dim harmonic oscillators each  $q_i$  or  $p_i$  has  $\langle E_i \rangle = \frac{kT}{2}$ , so  $\langle E \rangle = 2N \frac{kT}{2} = N kT$ , and so on. However equipartition is a classical result: it corresponds to considering the spacing of quantum energy levels  $\Delta E \ll kT$ , so that energy can be considered as continuous. So no problem for translations, but vibrations at low  $T$  do not follow equipartition...

One can also prove, for generic  $H$ ,  $\langle x_i \frac{\partial H}{\partial x_j} \rangle = kT \delta_{ij}$  ( $\rightarrow$  equipart...)

both in microcan. ens. (Tuckerman 3.3) and canonical ens.

# **TD8**

## N DISTINGUISHABLE HARMONIC OSCILLATORS NVE

Consider another example: Oscillators that are distinguishable like atoms in a solid, vibrating independently from each other, well-localized on lattice sites.

$$H = \sum_i^N \left( \frac{p_i^2}{2m} + \frac{1}{2} mw^2 q_i^2 \right) \quad \kappa = mw^2, \quad w = \sqrt{\frac{\kappa}{m}}$$

as for ideal gas,  $\Omega = \frac{1}{h^N} [V(H < E + \delta E) - V(H < E)] = n(H < E + \delta E) - n(H < E)$  where we lack the term  $\frac{1}{N!}$  because oscillators are distinguishable.

$$H < E \Rightarrow \sum (p_i^2 + (mwq_i)^2) = \sum (p_i^2 + \tilde{q}_i^2) < 2mE$$

$$\tilde{q}_i = mwq_i, \quad dq_i = d\tilde{q}_i/mw :$$

pag. 53

$$n(H < E) = \frac{1}{h^N} \frac{1}{(mw)^N} \int_{\sum (p_i^2 + \tilde{q}_i^2) < 2mE} d\tilde{q}^N d^N p \quad (\text{zN-dim volume of hypersphere}) \\ = \frac{1}{(h\pi)^N} \frac{\pi^{2N/2}}{\left(\frac{2N}{2}\right)!} (\sqrt{2mE})^{2N} = \frac{1}{N!} \left(\frac{2\pi}{h\omega}\right)^N E^N = \frac{1}{N!} \left(\frac{E}{\hbar\omega}\right)^N$$

where this  $N!$  does not come from indistinguishability!

$$\Omega = n(H < E + \delta E) - n(H < E) = \frac{1}{N! (\hbar\omega)^N} [(E + \delta E)^N - E^N] \approx \\ \approx \frac{1}{N!} \left(\frac{E}{\hbar\omega}\right)^N N \frac{\delta E}{E}$$

$$\log \Omega \approx -N \log N + N + N \log \left(\frac{E}{\hbar\omega}\right) + \log \left(N \frac{\delta E}{E}\right)$$

where the last term is the only non-extensive one (see pag. 54)

$$\Rightarrow \log \Omega \approx \log n(H < E) = N \left( 1 + \log \left( \frac{E}{N\hbar\omega} \right) \right), \quad S = k \log \Omega$$

$$\frac{1}{T} = \left( \frac{\partial S}{\partial E} \right)_N = \frac{N\kappa}{E}, \quad E = N\kappa T \quad (\text{equipartition...})$$

$$\mu = -T \left( \frac{\partial S}{\partial N} \right)_E = \kappa T \log \left( \frac{N\hbar\omega}{E} \right) = \kappa T \log \left( \frac{\hbar\omega}{\kappa T} \right)$$

by repeating the calculation in the quantum case one has

$$E = \sum_i^N \left( n_i + \frac{1}{2} \right) \hbar\omega = \left( M + \frac{N}{2} \right) \hbar\omega$$

and  $\Omega$  is the number of ways of choosing  $N$  positive integers  $n_i$  in such a way as  $\sum n_i = M \dots \Omega = (N+M-1)! / M!(N-1)!$

... one finds that the classical results correspond to the limit  $kT \gg \hbar\omega$  (see course of Haugset).

## N DISTINGUISHABLE HARMONIC OSCILLATORS

NVT

We reconsider the case treated at page 58 in the microcan ensemble: first consider a single 1-dim harmonic osc.:

$$H = \frac{P^2}{2m} + \frac{1}{2} m \omega^2 x^2$$

$$Z = \frac{1}{h} \int dx dp e^{-\beta H} = \frac{1}{h} \int_0^L dx e^{-(\beta m \omega^2/2)x^2} \int_{-\infty}^{\infty} dp e^{-(\beta/2m)p^2}$$

where we consider a box of size  $L$ , and we can replace with  $\int_{-\infty}^{\infty} dx$  if the width of  $e^{-(\beta m \omega^2/2)x^2}$  is small compared to  $L$ :

$$Z = \frac{1}{h} \sqrt{\frac{2\pi}{\beta m \omega^2}} \sqrt{\frac{2\pi m}{\beta}} = \frac{2\pi}{\beta \hbar \omega} = \frac{1}{\beta \hbar \omega}$$

thus for  $N$  (uncoupled) distinguishable harmonic oscillators:

$$Z = Z^N = \left( \frac{1}{\beta \hbar \omega} \right)^N = \left( \frac{kT}{\hbar \omega} \right)^N$$

$$\langle E \rangle = -\frac{\partial}{\partial \beta} \log Z = -\frac{\partial}{\partial \beta} [-N \log(\beta \hbar \omega)] = \frac{N}{\beta} = NkT \quad (\text{same as pag. 58})$$

$$C_V = \left( \frac{\partial \langle E \rangle}{\partial T} \right)_V = Nk, \quad \frac{\sigma_E}{\langle E \rangle} = \frac{\sqrt{kT^2 C_V}}{NkT} = \frac{\sqrt{Nk^2 T^2}}{NkT} = \frac{1}{\sqrt{N}}$$

3)  $Z = Z^N = (1 + e^{-\beta E})^N$  (distinguishables) | TD8

$$\langle E \rangle = -\frac{\partial}{\partial \beta} \log Z = -N \frac{(-E)e^{-\beta E}}{1 + e^{-\beta E}} = NE \frac{x}{1+x}, \quad x = e^{-\beta E}$$

$$F = -kT \log Z = -NkT \log(1+x)$$

$$S = \frac{\langle E \rangle - F}{T} = N \left( \frac{E}{T} \frac{x}{1+x} + k \log(1+x) \right)$$

$$\frac{\langle E \rangle}{N} = \frac{Ex}{1+x}$$

- low T:  $x \rightarrow 0$ ,  $\langle E \rangle/N \rightarrow 0$
- high T:  $x \rightarrow 1$ ,  $\langle E \rangle/N \rightarrow E/2$

$$\frac{S}{N} = k \left( \beta E \frac{x}{1+x} + \log(1+x) \right)$$

- low T:  $x \rightarrow 0$ ,  $\frac{S}{N} \rightarrow 0$
- high T:  $x \rightarrow 1$ ,  $\frac{S}{N} \rightarrow k \log 2$
- $\beta \rightarrow 0$  like NVE!

Scanné avec CamScanner

## Capacité calorifique d'un solide

✓

$$3N \text{ osc. HARM } \omega \xrightarrow{\text{Equip}} \langle E \rangle = 3N k_B T$$

$$\boxed{C = \frac{\partial E}{\partial T} = 3N k_B} \quad \text{Dulong et Petit}$$

### \* osc. QUANTIQUE

$$\text{donc: } E = k\omega \left(\frac{1}{2} + m_x\right) + k\omega \left(\frac{1}{2} + m_y\right) + k\omega \left(\frac{1}{2} + m_z\right)$$

$$Z = z^N = (z_x z_y z_z)^N = z_{1D}^{3N}$$

$$\begin{aligned} z_{1D} &= \sum_{m=0}^{\infty} e^{-\beta E_m} = e^{-\beta \frac{k\omega}{2}} \sum_m e^{-\beta k\omega m} \\ &= e^{-\beta \frac{k\omega}{2}} \sum_m (e^{-\beta k\omega})^m \quad \text{avec } x = \beta k\omega \end{aligned}$$

$$z_{1D} = \frac{e^{-\beta \frac{k\omega}{2}}}{1 - e^{-\beta k\omega}}$$

pour un oscillateur 3D

$$\boxed{Z = \frac{e^{-\frac{3}{2}\beta k\omega}}{(1 - e^{-\beta k\omega})^3}}$$

pour N osc. 3D  $\boxed{Z = z^N}$

$$\langle E \rangle = -\frac{\partial}{\partial \beta} \ln Z = -N \frac{\partial}{\partial \beta} \ln z$$

$$\langle E \rangle = N \frac{\partial}{\partial \beta} \left[ \frac{3}{2} \beta \hbar \omega + 3 \ln (1 - e^{-\beta \hbar \omega}) \right]$$

$$\langle E \rangle = 3N \frac{\hbar \omega}{2} + 3N \hbar \omega \cdot \frac{e^{-\beta \hbar \omega}}{1 - e^{-\beta \hbar \omega}}$$

$$\boxed{\langle E \rangle = 3N \hbar \omega \left[ \frac{1}{e^{\beta \hbar \omega} - 1} + \frac{1}{2} \right]}$$

$$C = \frac{\partial \langle E \rangle}{\partial T} = + \frac{3N \hbar \omega}{k_B T^2} \frac{\hbar \omega e^{\beta \hbar \omega}}{(e^{\beta \hbar \omega} - 1)^2} = (\hbar \omega \beta)^2 \frac{3N k_B e^{\beta \hbar \omega}}{(e^{\beta \hbar \omega} - 1)^2}$$

$$\beta = \frac{1}{k_B T} ; \quad \frac{\partial}{\partial T} = \frac{\partial}{\partial \beta} \frac{\partial \beta}{\partial T} = -\frac{1}{k_B T^2} \frac{\partial}{\partial \beta}$$

$$\boxed{C = 3N k_B \frac{(\hbar \omega \beta)^2 e^{\beta \hbar \omega}}{(e^{\beta \hbar \omega} - 1)^2}}$$

$$\boxed{\Theta_E \equiv \frac{\hbar \omega}{k_B}}$$

K.B.  $T \rightarrow 0$ ;  $x = \frac{\hbar \omega}{k_B T} = \beta \hbar \omega \rightarrow +\infty$ ;  $C \propto x^2 e^{-x} \rightarrow 0$

$T \ll \Theta_E$   $T \rightarrow +\infty$ ;  $x = \frac{\hbar \omega}{k_B T} = \beta \hbar \omega \rightarrow 0$ ;  $C \rightarrow 3N k_B$

$T \gg \Theta_E$

en effet  $\frac{x^2 e^x}{(e^x - 1)^2} \rightarrow 1$

$$(x + x + x^2 + \dots - 1)^2 = x^2 + \dots$$

# TD9

(1.1)

$$\frac{P_A}{P_B} = \frac{t_A}{t_B} \quad (\text{we suppose good equilibration, ergodicity})$$

$\approx \frac{10}{30}$ ,  $P_A = 0.25$   
 $P_B = 0.75$

TD9

$$K_{A \rightarrow B} = \frac{N_{A \rightarrow B}}{t_A} \equiv \frac{1}{T_{AB}} \approx \frac{8}{10 \text{ ns}} = 0.8 \text{ ns}^{-1}$$

$T_{AB}$  mean first passage time

$$K_{B \rightarrow A} = \frac{N_{B \rightarrow A}}{t_B} \equiv \frac{1}{T_{BA}} \approx \frac{8}{30 \text{ ns}} = 0.27 \text{ ns}^{-1}$$

Note that:  $P_A K_{A \rightarrow B} = P_B K_{B \rightarrow A}$  (detailed balance, because, in general (i.e., at equil. or out-of-equil.) see TD on master eq.)

$$\frac{K_{AB}}{K_{BA}} = \frac{P_B}{P_A} \quad \left\{ \begin{array}{l} \dot{P}_A = P_B K_{BA} - P_A K_{AB} \\ \dot{P}_B = P_A K_{AB} - P_B K_{BA} \end{array} \right. \begin{array}{l} \text{equil: } \dot{P}_A = 0 \\ \dot{P}_B = 0 \end{array}$$

(1.2)

Important: A & B are macrostates (because, visually, many E values for same state), not microstates, therefore

$$\frac{P_A}{P_B} = \frac{e^{-\beta F_A}}{e^{-\beta F_B}} \quad \left( \text{not } \frac{P_A}{P_B} = \frac{e^{-\beta E_A}}{e^{-\beta E_B}} \text{ common mistake!} \right)$$

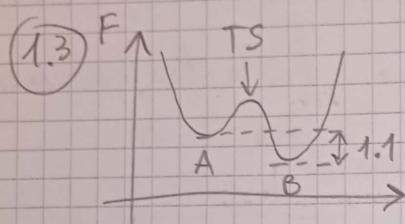
$$F_A = -kT \log Z_A \leftarrow \text{partition function} \quad \sum_{i \in A} e^{-\beta E_i}$$

$$\frac{P_A}{P_B} = \frac{Z_A}{Z_B}, \quad F_B - F_A \equiv \Delta F_{AB} = -kT \log \frac{P_B}{P_A} = -1.1$$

$$\Delta E_{AB} (\text{visually}) \approx -4, \quad TAS_{AB} = \Delta E - \Delta F \approx -2.9 \quad (1)$$

$\Rightarrow S_A > S_B$ : counterintuitive (maybe), but true because  $\Delta F_{AB}$  is in favor of B only by little, while  $\Delta E_{AB}$  is too much in favor of B, it should give a much more probable B if one would apply.

$P_{A/B} \propto e^{-\beta E_{A/B}}$  ← (wrong because A & B are not microstates) In conclusion, he explain the little preference for B despite of a large energy preference, entropy must play again.



transition state identification:  
all microstates in phase space such that trajectories starting from them with thermal (Maxwell-Boltzmann) velocities have 50% chance to fall in A or B.

If Q is a good order param (reaction coord), then the barrier top in  $F(Q)$  should contain only TS configurations (note that a point in Q space corresponds to many points in phase space, since we projected (coarse grained) from  $3N$  coordinates to 1 coordinate). Otherwise we conclude that Q is not a good order parameter.

(1.4) Assuming a very long, ergodic trajectory  $q(t)$

$$p(Q) = \frac{1}{t_{TOT}} \int dt \delta(f(\vec{r}_1(t), \dots, \vec{r}_N(t)) - Q)$$

prob. density
Dirac function defining Q
specific value Q

explanation: time spent in  $[Q, Q+dQ]$  vs total time  
 $\int dQ p(Q) = 1$

in practice, real trajectory is discretized in time:  
 $s(t_i)$        $t_0, t_1, \dots$

$$\{Q(t_i)\}_{i=1,\dots,M}, \quad t_{i+1} - t_i = st \quad \forall i$$

$$p(q) = \frac{1}{M} \sum_{i=1}^M \chi_q(q(t_i)) \quad \text{"histogram of } q \text{"}$$

$$F(Q) = -kT \log P(Q) \quad \text{finite width}$$

In the form of ensemble-like formulas:

$$F(Q) = -kT \log p(Q),$$

$$p(Q) = \frac{\int d^3N r \int d^3N p e^{-\beta H} \delta(f(\vec{r}_1, \dots, \vec{r}_N) - Q)}{\int d^3N r \int d^3N p e^{-\beta H}}$$

This is the marginal prob. density (check:  $\int d\theta p=1$ )

In a simple case  $R \equiv r_{1x}$ :

$$p(r_{1x}) = \frac{\int dr_{1y} \int dr_{1z} \int_{-\infty}^N d\vec{r}_i \int d^3N p e^{-\beta H}}{\int d^3N r \int d^3N p e^{-\beta H}}$$

(as def. of marginal prob.) ( $\int dx_1 \times p = 1$ )

Take-home message: we need marginal price.

as a function of  $Q$ ; in real life: from histogram.

③ QEF is ok (e.g.  $U$  is good order param for crystallization)

①.5) trajectorye  $(Q_1(t), Q_2(t)) \rightarrow$  histogram  
 $\rightarrow F(\vec{Q}) = -kT \log p(\vec{Q})$  line before,  $\vec{Q}$  is 2.  
 (the full trajectory being  $(\vec{r}(t), \vec{p}(t))$  with  
 $\vec{r}, \vec{p}$  3N dim.)

$$p(Q_1, Q_2) = C \cdot e^{-\beta F(Q_1, Q_2)} \Rightarrow$$

$\uparrow$   
 irrelevant  
 normalization  
 constant

$$\tilde{p}(Q_1) = \int dQ_2 p(Q_1, Q_2) = C \int dQ_2 e^{-\beta F(Q_1, Q_2)}$$

and similar for  $Q_2$ .

$$\tilde{F}(Q_1) = -kT \log \tilde{p}(Q_1)$$

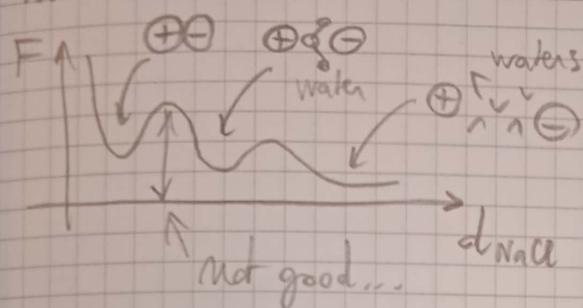
(always:  $F$  landscape  
 is within a shifting  
 constant, irrelevant  
 because we care about  
 variations)

Important:  $Q_1(t)$  et  $Q_2(t)$  look similar,  
 but quantitative difference is that  $Q_1$  resolves  
 well than  $Q_2$  the two metastable states,  
 because when we project probability along  
 $Q_1$  we see clearly the two "mountains" A and b  
 with a gap in between (transition state region),  
 while projecting along  $Q_2$  gives more overlap  
 (check graph of  $F(Q_1, Q_2)$ ).

④ We see barrier if overlap between peaks is zero  
 (a weak)

otherwise the barrier disappears. It is just a geometric effect, but important: it discriminates between good and bad order param/ reaction coord.

Example from research: if you have Na Cl (pair) in water (traj. on moodle), Na-Cl distance is obvious order param. distinguishing 3 metastable states:



but it is not optimal, because we neglected d.o.f. of water, thus barrier is too low and in the barrier top we mix TS configuration with non-TS ones.

Similarly, for crystal nucleation  $\mathcal{V}$  (pot. energy) can be a good order param., but not the optimal one, because also other information missing in  $\mathcal{V}$  can be relevant. An open problem!

Same problem in chemical reactions, protein folding, protein-drug dissociation etc.

$$\begin{aligned} \textcircled{2} \quad A_i &\equiv A(t_i), \quad i=1, \dots, n : & j &= 0, \dots, k \\ c(t) &= \frac{\langle (A(t) - \langle A \rangle)(A(0) - \langle A \rangle) \rangle}{\text{Var}(A)} \approx c_j \equiv c(t_j) = \\ & \sum_{i=1}^{n-k} (A_{i+j} - \langle A \rangle)(A_i - \langle A \rangle) / \text{Var}(A) && \begin{array}{l} \text{(hypothesis: stationary} \\ \text{statistics)} \end{array} \\ & \langle A \rangle \approx \frac{1}{n} \sum A_i, \quad \text{Var}(A) \approx \frac{1}{n} \sum A_i^2 - \left( \frac{1}{n} \sum A_i \right)^2 \end{aligned} \quad \boxed{5}$$

## TD10

$$1) \frac{dp}{dT} = \frac{\ell \leftarrow \text{melting}}{T \Delta V} = \frac{6050 \text{ J/mol}}{273 \cdot (-4.5 \cdot 10^{-6}) \text{ m}^3/\text{mol}} = -4.8 \cdot 10^6 \frac{\text{J}}{\text{m}^3 \text{K}} \left( \frac{\text{Pa}}{\text{K}} \right)$$

$\Delta V =$

$$\Rightarrow \Delta P(0^\circ\text{C} \rightarrow -2^\circ\text{C}) = \frac{dp}{dT} \Delta T = -4.8 \cdot 10^6 (-2) \text{ Pa} = 9.6 \cdot 10^6 \text{ Pa} \approx 10^7 \text{ Pa}$$

$$\Delta p = \frac{Mg}{S}, \quad M = \frac{\Delta p \cdot S}{g} = \frac{10^7 \cdot 10^{-4}}{9.8} \approx 100 \text{ kg}$$

$$\downarrow$$

$$= \frac{\rho S Hg}{S} = \rho Hg, \quad H = \frac{\Delta p}{\rho g} = \frac{10^7}{7800 \cdot 9.8} = 130 \text{ m (!)}$$

$$(V = S \cdot H = 10^{-4} \cdot 130 = 0.013 \text{ m}^3 \dots \text{ ok!})$$

Note: 1 atm = 101 325 Pa.

# TD11

①

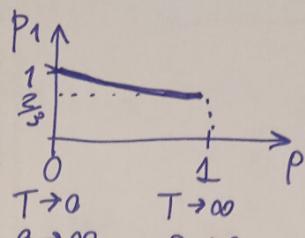
$$p = e^{-\beta \epsilon}$$

| $n$ | 1          | 2           | 3           |
|-----|------------|-------------|-------------|
| $E$ | $\epsilon$ | $2\epsilon$ | $3\epsilon$ |

STAT PHYS 10/01/22

$$Z_1(p) = p + p^2 + p^3$$

$$p_1(p) = \frac{p + p^3}{Z} = \frac{1 + p^2}{1 + p + p^2}$$



at low  $T$   $n=2$  is empty

because not ground state;  $(\sim \frac{1}{1+p}) (\frac{2}{3})$

at high  $T$  each state

has  $1/3$  occupation since

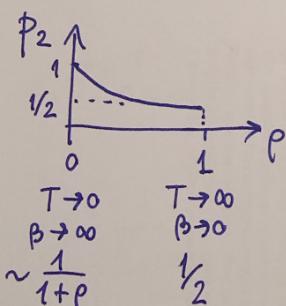
$kT \gg \epsilon$

2) Bosons:

$$\begin{array}{l} |11\rangle |12\rangle |13\rangle \\ \text{GS} \quad |22\rangle |23\rangle \\ \quad |33\rangle \end{array}$$

$$Z_2^B = p^2 + p^3 + 2p^4 + p^5 + p^6$$

$$p_2^B = \frac{p^2 + p^4 + p^6}{Z} = \frac{1 + p^2 + p^4}{1 + p + 2p^2 + p^3 + p^4} = 1 - \frac{p^3 + p^4 + p^5}{Z}$$



low  $T \rightarrow$  ground state w/o  $n=2$

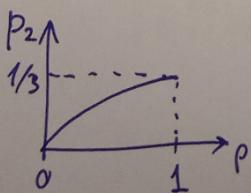
high  $T \rightarrow$  six states w equal pop  
(half w  $n=2$ )

Fermions:

$$\begin{array}{l} |12\rangle |23\rangle |13\rangle \\ \text{GS} \end{array}$$

$$Z_2^F = p^3 + p^4 + p^5$$

$$p_2^F = \frac{p^4}{Z} = \frac{p}{1 + p + p^2} = 1 - \frac{p^3 + p^5}{Z}$$



low  $T \rightarrow$  ground state w  $n=2$

high  $T$ : 3 states with equal pop  
(2 w  $n=2$ )

# TD12

## References

- [1] Peter Atkins and Julio de Paula. *Physical chemistry: thermodynamics, structure, and change*. WH Freeman and Company New York, 2014.