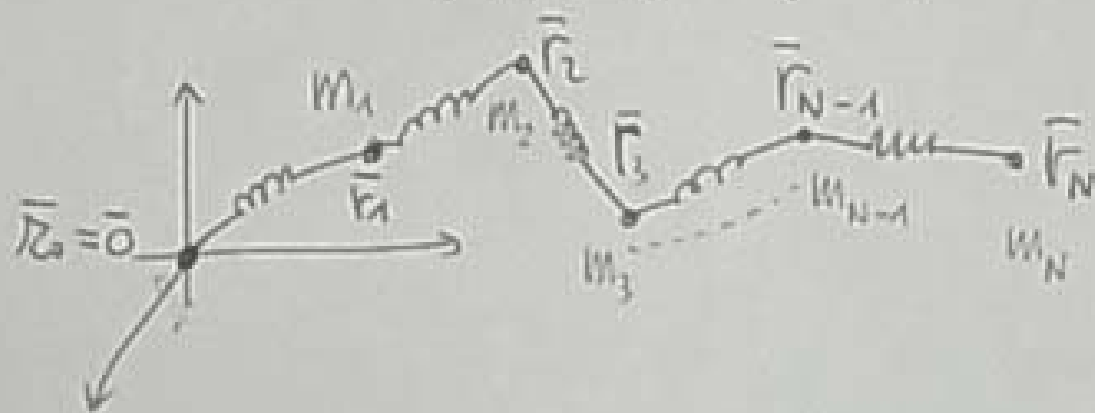


From statistical mechanics to thermodynamics of a polymeric chain

①

We consider a chain of atoms (or molecules intended as single entities) characterized by positions \vec{r}_i ($i=1..N$) and momenta \vec{p}_i ($i=1..N$).

We suppose the chain fixed at the position $\vec{r}_0 \equiv (0,0,0)$ (to fix the ideas):



We also suppose that the dynamics of the system is governed by an arbitrary interaction potential energy $V = V(\vec{r}_1, \dots, \vec{r}_N)$, which describes all the forces exerted among all the entities of the chain.

Therefore, the dynamics of the system ②
is described by an Hamiltonian:

$$h(\bar{r}_1 \dots \bar{r}_N, \bar{p}_1 \dots \bar{p}_N) = \sum_{i=1}^N \frac{\bar{p}_i \cdot \bar{p}_i}{2m_i} + V(\bar{r}_1 \dots \bar{r}_N) \quad [1]$$

(We use h to identify the Hamiltonian since the symbol H will be used for enthalpies later on).

Moreover, we consider this system in contact with (immersed or embedded to) a thermal bath characterized by a temperature T . It means that, at thermal equilibrium, the density probability in phase space is described by the well-known Gibbs distribution

$$\rho(q, p) = \frac{1}{Z} e^{-\frac{h(q, p)}{kT}} \quad [2]$$

where $q = (\bar{T}_1 \dots \bar{T}_N)$, $p = (\bar{p}_1 \dots \bar{p}_N)$ ③
and Z is the canonical partition function.

$$Z = \iint_{\Gamma} e^{-\frac{h(q,p)}{kT}} dq dp \quad [3]$$

where Γ is the phase space, here considered as \mathbb{R}^{6N} (since $q \in \mathbb{R}^{3N}$ and $p \in \mathbb{R}^{3N}$). The convergence, at thermal equilibrium, to the Gibbs distribution is the only notion not proved in the present note: all the consequences will be demonstrated with many details. The main goal of this note is to obtain the macro- or meso-scopic thermodynamic quantities of the system starting from the above stated Gibbs distribution.

To this aim we follow two dual approaches that are equivalent in the limit of a large system (thermodynamic limit). ④

In the first approach we suppose to fix the position \bar{r}_N of the last component of the chain and we define $\bar{r} \equiv \bar{r}_N$ as a macroscopic variable. This case is similar to that of an ideal gas maintained in a given volume V .

In the second approach we suppose to apply a given force \vec{f} to the last particle and we consider \vec{f} as a macroscopic variable. This case

is similar to that of a gas
constrained with a given pressure P .

(5)

First approach (Helmholtz ensemble)

The position $\bar{r} \equiv \bar{r}_N$ is fixed and,
therefore, we use an Hamiltonian:

$$h = h \left(\underbrace{\bar{r}_1 \dots \bar{r}_{N-1}}_q, \underbrace{\bar{p}_1 \dots \bar{p}_{N-1}}_p; \underbrace{\bar{r}_N}_{\bar{r}} \right) \quad [4]$$

In this case the microscopic variables
are $q = (\bar{r}_1, \dots, \bar{r}_{N-1})$ and $p = (\bar{p}_1, \dots, \bar{p}_{N-1})$ and
we obtain:

$$Z = Z(\bar{r}, T) = \int \int_{\Gamma} e^{-\frac{h(q, p, \bar{r})}{kT}} dq dp \quad [5]$$

where $\Gamma = \mathbb{R}^{6(N-1)}$. The Gibbs distribution is

$$p = p(q, p, \bar{r}, T) = \frac{1}{Z} e^{-\frac{h(q, p, \bar{r})}{kT}} \quad [6]$$

The force exerted on $\bar{r} \equiv \bar{r}_N$ by the other components of the chain is (6)

$-\frac{\partial h}{\partial \bar{r}_N}$ by definition of interaction potential energy. Its mean value defines the macroscopic force and the constitutive equation of the chain.

In fact, the force exerted on the system (from outside) is:

$$\bar{f} = \left\langle \frac{\partial h}{\partial \bar{r}_N} \right\rangle = \iint_{\Gamma} \frac{\partial h}{\partial \bar{r}} \rho \, dq dp \quad [7]$$

or, equivalently:

$$\bar{f}(\bar{r}, T) = \frac{\iint_{\Gamma} \frac{\partial h(q, p, \bar{r})}{\partial \bar{r}} e^{-\frac{h(q, p, \bar{r})}{kT}} \, dq dp}{\iint_{\Gamma} e^{-\frac{h(q, p, \bar{r})}{kT}} \, dq dp} \quad [8]$$

We can say that this is the statistical Hooke law of the chain: $\bar{f} = \bar{f}(\bar{r}, T)$.

We also remark that this constitutive equation can be directly obtained by the partition function Z , in fact, from eq. [5] we obtain.

$$\frac{\partial Z}{\partial F} = \int e^{-\frac{h(q,p,\bar{F})}{kT}} \left(-\frac{1}{kT}\right) \frac{\partial h(q,p,\bar{F})}{\partial \bar{F}} dq dp \quad [9]$$

By combining eqs [8] and [9] we have

$$\bar{p}(\bar{F}, T) = -kT \frac{1}{Z} \frac{\partial Z}{\partial \bar{F}} = -kT \frac{\partial}{\partial \bar{F}} \ln Z \quad [10]$$

In addition to the constitutive equation the statistical mechanics also furnishes the macroscopic thermodynamics as follows. We consider the average value of the Hamiltonian as the internal energy of the system

(8)

$$\begin{aligned} U &= \langle h(q, p, \bar{F}) \rangle = \\ &= \iint_{\Gamma} h(q, p, \bar{F}) \rho(q, p, \bar{F}, T) dq dp = \\ &= \frac{\iint_{\Gamma} h(q, p, \bar{F}) e^{-\frac{h(q, p, \bar{F})}{kT}} dq dp}{\iint_{\Gamma} e^{-\frac{h(q, p, \bar{F})}{kT}} dq dp} \quad [11] \end{aligned}$$

In order to introduce the thermodynamics we must consider a transformation of the system. It means that the end-position $\bar{F} = \bar{F}(t)$ can vary with time and also the temperature $T = T(t)$ is a dynamical variable. In general, these assumptions lead to the out-of-equilibrium statistical mechanics. However, we assume a very slow motion of \bar{F} and T and, therefore,

we may say that the system evolves (9)
 through a quon-static transformation.
 A quon-static transformation passes
 through a sequence of equilibrium states
 and thus the dynamical probability
 density in the phase space is simply
 given by:

$$\rho(q, p, \bar{F}(t), T(t)) = \frac{1}{Z} e^{-\frac{h(q, p, \bar{F}(t))}{kT(t)}} \quad [12]$$

when Z is given by Eq (5) with
 $\bar{F} = \bar{F}(t)$ and $T = T(t)$ -

With these hypotheses we can try to
 obtain $\frac{dU}{dt}$ starting from Eq (11).

The time intervenes only through \bar{F} and T .

$$\frac{dU}{dt} = \int \int \frac{d}{dt} [h(q, p, \bar{F}(t)) \rho(q, p, \bar{F}(t), T(t))] dq dp =$$

(10)

$$\begin{aligned}
 &= \int_{\Gamma} \frac{dh(q, p, F(t))}{dt} \int (q, p, \bar{F}(t), T(t)) dq dp + \quad \nearrow A \\
 &+ \int_{\Gamma} h(q, p, F(t)) \frac{d \int (q, p, \bar{F}(t), T(t))}{dt} dq dp \quad \nearrow B \quad [13]
 \end{aligned}$$

Now we are able to identify the first integral A with the work made on the system and the second integral B with the heat entering the system.

For A we obtain:

$$\begin{aligned}
 A &= \int_{\Gamma} \frac{\partial h(q, p, F)}{\partial \bar{F}} \cdot \frac{d\bar{F}}{dt} \int (q, p, \bar{F}, T) dq dp = \\
 &= \frac{d\bar{F}}{dt} \cdot \int_{\Gamma} \frac{\partial h(q, p)}{\partial \bar{F}} \int (q, p, \bar{F}, T) dq dp = \\
 &= \bar{f} \cdot \frac{d\bar{F}}{dt} \quad [14]
 \end{aligned}$$

having considered Eq. [7] or [8] -

The product force - velocity is the power, i.e. the work made for unit of time.

(11)

It means that: $A = \frac{dL}{dt}$ [15]

For the second integral B we elaborate the Gibbs distribution as follows:

$$\rho = \frac{e^{-\frac{h}{kT}}}{\int e^{-\frac{h}{kT}} dq dp} = e^{\frac{F-h}{kT}} \quad [16]$$

Where F is called Helmholtz free energy and it is linked to the partition function by

$$\frac{1}{Z} = e^{\frac{F}{kT}} \quad [17]$$

or, equivalently:

$$F = -kT \ln Z \quad [18]$$

For brevity we indicate $\eta = \frac{F-h}{KT}$
 and therefore $\rho = e^\eta$. The
 integral B assumes the form:

$$B = \iint_{\Gamma} h \frac{d\rho}{dt} dq dp =$$

$$= \iint_{\Gamma} h \frac{de^\eta}{dt} dq dp = \iint_{\Gamma} h e^\eta \dot{\eta} dq dp \quad [19]$$

Since $\iint_{\Gamma} \rho dq dp = 1$ we have

$$\iint_{\Gamma} e^\eta dq dp = 1 \text{ and we obtain}$$

$$\frac{d}{dt} \iint_{\Gamma} e^\eta dq dp = \iint_{\Gamma} e^\eta \dot{\eta} dq dp = 0 \quad [20]$$

Again, since F does not depend on p and q,
 we have:

$$\iint_{\Gamma} F e^\eta \dot{\eta} dq dp = 0 \quad [21]$$

So, we may write:

(13)

$$B = \iint_{\Gamma} (h - \bar{F}) e^{\eta} \dot{\eta} dq dp \quad [22]$$

When, however, $h - \bar{F} = -KT\eta$; then:

$$B = - \iint_{\Gamma} KT \eta \dot{\eta} e^{\eta} dq dp \quad [23]$$

To better understand the meaning of the previous integral we may calculate $\langle \eta \rangle$.

$$\langle \eta \rangle = \iint_{\Gamma} \eta \rho dq dp = \iint_{\Gamma} \eta e^{\eta} dq dp \quad [24]$$

and the variation of $\langle \eta \rangle$ with time:

$$\frac{d\langle \eta \rangle}{dt} = \iint_{\Gamma} \dot{\eta} e^{\eta} dq dp + \iint_{\Gamma} \eta e^{\eta} \dot{\eta} dq dp \quad [25]$$

The first term is zero because of
Eq. [20], so:

$$B = -kT \frac{d}{dt} \langle \eta \rangle \quad [26]$$

Since B is interpreted as the heat given to the system for unit of time we have obtained

$$B = \frac{dQ}{dt} = T \frac{dS}{dt} \quad [27]$$

where we have introduced the entropy.

$$S = -k \langle \ln \rho \rangle = -k \int \rho \ln \rho \, dq \, dp \quad [28]$$

In conclusion we have obtained the first and the second principles starting simply from the Gibbs distribution.

$$\frac{dU}{dt} = \frac{dL}{dt} + \frac{dQ}{dt} \quad [29] \quad (\text{1st principle})$$

when

$$\frac{dL}{dt} = \vec{f} \cdot \frac{d\vec{r}}{dt} \quad [30] \quad (\text{work})$$

and

$$\frac{dQ}{dt} = T \frac{dS}{dt} \quad [31] \quad (\text{heat, 2nd principle})$$

From the relation $h - F = -kT \eta$ we perform the average and we obtain $U - F = TS$ from which:

$$F = U - TS \quad [32]$$

This is the standard definition in classical thermodynamics.

Further, from Eq (10) and (17), we have:

$$\vec{f} = -kT \frac{\partial \ln Z}{\partial \vec{r}} = \frac{\partial F(F, T)}{\partial \vec{r}} \quad [33]$$

which is a simple form for the constitutive equation.

Several thermodynamic relations follow from the above scheme:

(16)

eq. [23] is written as

$$dU = \vec{f} \cdot d\vec{F} + T dS \quad [34]$$

if $U = U(\vec{F}, S)$ we obtain

$$\vec{f} = \frac{\partial U}{\partial \vec{F}} \quad \text{and} \quad T = \frac{\partial U}{\partial S} \quad [35]$$

from eq. [32] we obtain

$$\begin{aligned} dF &= dU - T dS - S dT = \\ &= \vec{f} \cdot d\vec{F} + T dS - T dS - S dT = \\ &= \vec{f} \cdot d\vec{F} - S dT \end{aligned} \quad [36]$$

if $F = F(\vec{F}, T)$ we have

$$\vec{f} = \frac{\partial F}{\partial \vec{F}} \quad \text{and} \quad S = - \frac{\partial F}{\partial T} \quad [37]$$

The classical thermodynamics of a gas or a fluid is obtained by substituting \vec{F} and \vec{f} with volume V and pressure P , respectively.

Second approach (Gibbs ensemble)

(17)

We suppose now to consider a given applied force \bar{f} to the particle placed at \bar{r}_N . This force can be introduced by means of an additional potential energy $-\bar{f} \cdot \bar{r}_N$ (so that $-\frac{\partial}{\partial \bar{r}_N} (-\bar{f} \cdot \bar{r}_N) = \bar{f}$ as requested)

therefore the system is described by the so-called augmented Hamiltonian

$$\begin{aligned} \tilde{h}(\bar{r}_1, \dots, \bar{r}_N, \bar{p}_1, \dots, \bar{p}_N, \bar{f}) = \\ = h(\bar{r}_1, \dots, \bar{r}_N, \bar{p}_1, \dots, \bar{p}_N) - \bar{f} \cdot \bar{r}_N \quad [30] \end{aligned}$$

The quantities $q = (\bar{r}_1, \dots, \bar{r}_N)$ and

$p = (\bar{p}_1, \dots, \bar{p}_N)$ are the microscopic

variables while \bar{f} assumes the role of the macroscopic variable.

The partition function is:

(18)

$$\bar{Z} = Z(\bar{f}, T) = \iint_{\Gamma} e^{-\frac{\tilde{h}(q, p, \bar{f})}{kT}} dq dp \quad [39]$$

And the corresponding Gibbs distribution

$$\rho(q, p, \bar{f}, T) = \frac{1}{\bar{Z}} e^{-\frac{\tilde{h}(q, p, \bar{f})}{kT}} \quad [40]$$

As before, we may determine the constitutive equation of the system: To this aim

we observe that $\partial \tilde{h} / \partial \bar{f} = -\bar{r}_0$ and therefore

we calculate the average position of the

head of the chain as $\bar{r} = \langle \bar{r}_0 \rangle$ or

more explicitly:

$$\bar{r} = - \left\langle \frac{\partial \tilde{h}}{\partial \bar{f}} \right\rangle = - \iint_{\Gamma} \frac{\partial \tilde{h}}{\partial \bar{f}} \rho dq dp \quad [41]$$

which is the counterpart of Eq. (7).

By using Eqs (39) and (40) i.e. Eq (41)

we obtain:

(19)

$$\bar{F}(\bar{f}, T) = - \frac{\iint \frac{\partial \tilde{h}(q, p, \bar{f})}{\partial \bar{f}} e^{-\frac{\tilde{h}(q, p, \bar{f})}{KT}} dq dp}{\iint e^{-\frac{\tilde{h}(q, p, \bar{f})}{KT}} dq dp} \quad [42]$$

which is the counterpart of Eq. (35). This constitutive equation can also be expressed by means of the partition function Z .

In fact, by differentiating Eq. (39) with respect to \bar{f} , we obtain

$$\frac{\partial Z}{\partial \bar{f}} = \iint e^{-\frac{\tilde{h}(q, p, \bar{f})}{KT}} \left(-\frac{1}{KT}\right) \frac{\partial \tilde{h}(q, p, \bar{f})}{\partial \bar{f}} dq dp \quad [43]$$

and, therefore:

$$\bar{F}(\bar{f}, T) = KT \frac{1}{Z} \frac{\partial Z}{\partial \bar{f}} = KT \frac{\partial}{\partial \bar{f}} \ln Z \quad [44]$$

Now, we may introduce the macroscopic thermodynamics by

identifying the average value of the augmented Hamiltonian with the enthalpy of the system.

$$H = \langle \tilde{h}(q, p, \bar{F}) \rangle =$$

$$= \iint_{\Gamma} \tilde{h}(q, p, \bar{F}) \rho(q, p, \bar{F}, T) dq dp =$$

$$= \frac{\iint_{\Gamma} \tilde{h}(q, p, \bar{F}) e^{-\frac{\tilde{h}(q, p, \bar{F})}{kT}} dq dp}{\iint_{\Gamma} e^{-\frac{\tilde{h}(q, p, \bar{F})}{kT}} dq dp} \quad [42]'$$

As before we suppose that $\bar{F} = \bar{F}(t)$ and $T = T(t)$ in order to introduce a quasi-static transformation. We develop the time derivative of the enthalpy:

$$\frac{dH}{dt} = \iint_{\Gamma} \frac{d}{dt} [\tilde{h}(q, p, \bar{F}) \rho(q, p, \bar{F}, T)] dq dp =$$

$$= \iint_{\Gamma} \frac{d\tilde{h}(q, p, \bar{F})}{dt} \rho(q, p, \bar{F}, T) dq dp + \quad \nearrow A$$

$$+ \iint_{\Gamma} \tilde{h}(q, p, \bar{F}) \frac{d\rho(q, p, \bar{F}, T)}{dt} dq dp \quad \nearrow B \quad [43]'$$

The first term is

(21)

$$\begin{aligned} A &= \int \int \frac{\partial \tilde{h}(q, p, \bar{E})}{\partial \bar{E}} \cdot \frac{d\bar{E}}{dt} \rho(q, p, \bar{E}, T) dq dp = \\ &= \frac{d\bar{E}}{dt} \cdot \int \int \frac{\partial \tilde{h}(q, p, \bar{E})}{\partial \bar{E}} \rho(q, p, \bar{E}, T) dq dp = \\ &= - \frac{d\bar{E}}{dt} \cdot \bar{\kappa} \quad [44]' \end{aligned}$$

The second term can be developed by introducing a new form of the Gibbs distribution

$$\rho(q, p, \bar{E}, T) = \frac{1}{Z} e^{-\frac{\tilde{h}}{KT}} = e^{\frac{G - \tilde{h}}{KT}} \quad [45]$$

where G is the Gibbs free energy:

$$\frac{1}{Z} = e^{\frac{G}{KT}} \quad \text{or} \quad G = -KT \ln Z \quad [46]$$

For brevity, as before, we indicate

$\hat{h} = \frac{G - \tilde{h}}{KT}$. We briefly repeat the calculation of B following the procedure starting

From Eq. (19). The integral B assumes the form.

(22)

$$B = \iint_{\Gamma} \tilde{h} \frac{d}{dt} e^{\tilde{h}} dq dp = \iint_{\Gamma} \tilde{h} \dot{\tilde{h}} e^{\tilde{h}} dq dp \quad [47]$$

Since $\iint_{\Gamma} e^{\tilde{h}} dq dp = 1$ we obtain:

$$\frac{d}{dt} \iint_{\Gamma} e^{\tilde{h}} dq dp = \iint_{\Gamma} e^{\tilde{h}} \dot{\tilde{h}} dq dp = 0 \quad [48]$$

and, since G is independent on q and p we can write

$$\iint_{\Gamma} G e^{\tilde{h}} \dot{\tilde{h}} dq dp = 0 \quad [49]$$

B can be therefore written also as:

$$\begin{aligned} B &= \iint_{\Gamma} (\tilde{h} - G) \dot{\tilde{h}} e^{\tilde{h}} dq dp = \\ &= - \iint_{\Gamma} KT \dot{\tilde{h}} \dot{\tilde{h}} e^{\tilde{h}} dq dp \quad [50] \end{aligned}$$

The average value of $\tilde{\eta}$ is given by $\langle \tilde{\eta} \rangle = \frac{\int \tilde{\eta} e^{-\tilde{\eta}} dq dp}{\int e^{-\tilde{\eta}} dq dp}$ and its time derivative is:

$$\begin{aligned} \frac{d\langle \tilde{\eta} \rangle}{dt} &= \frac{d}{dt} \left[\frac{\int \tilde{\eta} e^{-\tilde{\eta}} dq dp}{\int e^{-\tilde{\eta}} dq dp} \right] \\ &= \frac{\int \dot{\tilde{\eta}} e^{-\tilde{\eta}} dq dp - \int \tilde{\eta} \dot{e}^{-\tilde{\eta}} dq dp}{\int e^{-\tilde{\eta}} dq dp} \end{aligned} \quad [51]$$

From Eqs. (50) and (51) we obtain

$$B = -KT \frac{d}{dt} \langle \tilde{\eta} \rangle \quad [52]$$

Or, equivalently

$$B = T \frac{dS}{dt} = \frac{dQ}{dt} \quad [53]$$

where we have introduced the entropy

$$S = -K \langle \ln \rho \rangle = -K \int \rho \ln \rho dq dp \quad [54]$$

It is important to remark that Eq (54) is not identical to Eq (28) since the probability density ρ in the latter case corresponds to the Gibbs ensemble while, in the former case, it describes the Helmholtz ensemble. Only when the thermodynamic limit of a large system is satisfied, the two approaches yield the same results.

Anyway, the time derivative of the entropy has been obtained in the form

$$\frac{dH}{dt} = - \frac{d\bar{f}}{dt} \cdot \bar{x} + T \frac{dS}{dt} \quad [55]$$

Since

$$\frac{dU}{dt} = \bar{f} \cdot \frac{d\bar{x}}{dt} + T \frac{dS}{dt} \quad [56]$$

We obtain by subtraction:

[25]

$$\frac{dH}{dt} - \frac{dU}{dt} = -\frac{d\bar{f}}{dt} \cdot \bar{r} - \bar{f} \cdot \frac{d\bar{r}}{dt} = -\frac{d}{dt} (\bar{f} \cdot \bar{r})$$

[57]

or, equivalently:

$$H = U - \bar{f} \cdot \bar{r} \quad [58]$$

which is the standard definition of enthalpy in thermodynamics.

From the definition of $\tilde{\eta}$, namely

$G - \bar{h} = kT \tilde{\eta}$, we perform the averaging and we obtain $G - H = -TS$ or:

$$G = H - TS \quad [59]$$

which is the standard definition of Gibbs free energy. Moreover, from Eqs [44] and [46] we have

$$\bar{F} = kT \frac{\partial}{\partial \bar{f}} \ln Z = - \frac{\partial G(\bar{f}, T)}{\partial \bar{f}} \quad [60]$$

Some thermodynamic relations for enthalpy and Gibbs free energy follow:

(26)

From Eq [55] we have

$$dH = -\bar{\kappa} \cdot d\bar{f} + T dS \quad [61]$$

if $H = H(\bar{f}, S)$ we obtain

$$\bar{\kappa} = -\frac{\partial H}{\partial \bar{f}} \quad \text{and} \quad T = \frac{\partial H}{\partial S} \quad [62]$$

From Eq [59] we have

$$\begin{aligned} dG &= dH - T dS - S dT = \\ &= -\bar{\kappa} \cdot d\bar{f} + T dS - T dS - S dT = \\ &= -\bar{\kappa} \cdot d\bar{f} - S dT \end{aligned} \quad [63]$$

if $G = G(\bar{f}, T)$ we have:

$$\bar{\kappa} = -\frac{\partial G}{\partial \bar{f}} \quad \text{and} \quad S = -\frac{\partial G}{\partial T} \quad [64]$$

As before, the classical thermodynamics of a substance can be obtained by substituting $(\bar{\kappa}, \bar{f})$ with (V, P) -

Reptology

$$h = h(\bar{r}_1 - \bar{r}_N, \bar{p}_1 - \bar{p}_N)$$

(27)

Helmholtz ensemble

$\bar{p}_N = 0, \bar{r}_N$ fixed

$$h = h(\bar{r}_1 - \bar{r}_{N-1}, \bar{p}_1 - \bar{p}_{N-1}; \bar{r}_N)$$

$$= h(q, p, \bar{r})$$

$$Z_T(\bar{r}, T) = \int \int e^{-\frac{h(q, p, \bar{r})}{kT}} dq dp$$

$$P(q, p, \bar{r}, T) = \frac{1}{Z_T} e^{-\frac{h(q, p, \bar{r})}{kT}}$$

$$\bar{p} = \left\langle \frac{\partial h}{\partial \bar{r}} \right\rangle = -kT \frac{\partial}{\partial \bar{r}} \ln Z_T$$

\bar{r} macro, \bar{p} micro

Energy $U = \langle h \rangle$

$$\frac{dU}{dt} = \bar{p} \cdot \frac{d\bar{r}}{dt} + T \frac{dS}{dt}$$

$$\bar{F} = -kT \ln Z_T = F(\bar{r}, T)$$

Helmholtz free energy

$$\bar{p} = \frac{\partial F}{\partial \bar{r}}$$

$$F = U - TS$$

$$S = -k \langle \ln S \rangle$$

Gibbs ensemble

\bar{f} applied to \bar{r}_N

$$\tilde{h} = h(\bar{r}_1 - \bar{r}_N, \bar{p}_1 - \bar{p}_N) - \bar{f} \cdot \bar{r}_N$$

$$= \tilde{h}(q, p, \bar{f})$$

$$Z_f(\bar{f}, T) = \int \int e^{-\frac{\tilde{h}(q, p, \bar{f})}{kT}} dq dp$$

$$P(q, p, \bar{f}, T) = \frac{1}{Z_f} e^{-\frac{\tilde{h}(q, p, \bar{f})}{kT}}$$

$$\bar{r} = \left\langle -\frac{\partial \tilde{h}}{\partial \bar{f}} \right\rangle = kT \frac{\partial}{\partial \bar{f}} \ln Z_f$$

\bar{r} macro, \bar{f} micro

Enthalpy $H = \langle \tilde{h} \rangle$

$$\frac{dH}{dt} = -\frac{d\bar{f}}{dt} \cdot \bar{r} + T \frac{dS}{dt}$$

$$G = -kT \ln Z_f = G(\bar{f}, T)$$

$$\bar{F} = -\frac{\partial G}{\partial \bar{f}} \quad \text{Gibbs free energy}$$

$$G = H - TS$$

$$S = -k \langle \ln S \rangle$$

→ In the thermodynamic limit ←

$$\begin{cases} H = U - \bar{p} \cdot \bar{r} \\ G = F - \bar{f} \cdot \bar{r} \end{cases}$$

Relationship between $Z_T(\bar{r}, T)$ and $Z_F(\bar{r}, T)$

(28)

We recall the definitions of the partition functions of the two different ensembles.

$$Z_T(\bar{r}, T) = \int_{\Gamma} e^{-h(\bar{r}_1 - \bar{r}_{N-1}, \bar{p}_1, \dots, \bar{p}_{N-1}, \bar{r}) / kT} d\bar{r}_1 \dots d\bar{r}_{N-1} d\bar{p}_1 \dots d\bar{p}_{N-1} \quad [65]$$

$$Z_F(\bar{r}, T) = \int_{\Gamma} e^{-\frac{h(\bar{r}_1 - \bar{r}_N, \bar{p}_1, \dots, \bar{p}_N) - \bar{r} \bar{r}_N}{kT}} d\bar{r}_1 \dots d\bar{r}_N d\bar{p}_1 \dots d\bar{p}_N \quad [66]$$

We also remember that:

$$\int_{\mathbb{R}^3} \exp\left(-\frac{1}{2m kT} \bar{p} \cdot \bar{p}\right) d\bar{p} = (2\pi m kT)^{3/2} \quad [67]$$

It follows that:

$$\begin{aligned} Z_F(\bar{r}, T) &= \int_{\mathbb{R}^3} Z_T(\bar{r}, T) e^{+\frac{\bar{r} \cdot \bar{r}_N}{kT}} d\bar{r}_N \int_{\mathbb{R}^3} e^{-\frac{\bar{p}_N \cdot \bar{p}_N}{2m kT}} d\bar{p}_N = \\ &= (2\pi m kT)^{3/2} \int_{\mathbb{R}^3} Z_T(\bar{r}, T) e^{\frac{\bar{r} \cdot \bar{r}}{kT}} d\bar{r} \end{aligned}$$

and, therefore, we obtain:

(29)

$$Z_f(\bar{P}, T) = (2\pi\mu kT)^{3/2} \int_{\mathbb{R}^3} Z_r(\bar{r}, T) e^{\frac{\bar{p} \cdot \bar{r}}{kT}} d\bar{r}$$

[68]

It means that the Gibbs partition function is the three-dimensional Laplace (bilateral) transform of the Helmholtz partition function. (but for a multiplicative constant) -

there are two methods for inverting the previous integral transform.

1) Method based on the Fourier transform theory:

from Eq. [68] we introduce the imaginary argument $\bar{p} = -i\bar{q}$, so that:

$$Z_f(-i\bar{q}, T) = (2\pi\mu kT)^{3/2} \int_{\mathbb{R}^3} Z_r(\bar{r}, T) e^{-i\frac{\bar{q} \cdot \bar{r}}{kT}} d\bar{r}$$

Now, we have obtained a Fourier Transformation between $Z_f(-i\bar{q}, T)$ and $Z_r(\bar{r}, T)$.

Therefore, we may write:

$$\frac{Z_f(-i\bar{g}, T)}{(2\pi\omega KT)^{3/2}} = \int_{\mathbb{R}^3} Z_r(\bar{F}, T) e^{-i \frac{\bar{g} \cdot \bar{F}}{KT}} d\bar{F} \quad (3)$$

The Fourier transform follows the rules

$$\begin{cases} F(\bar{\omega}) = \int_{\mathbb{R}^3} f(\bar{r}) e^{-i \bar{\omega} \cdot \bar{r}} d\bar{r} & (3DFT) \end{cases}$$

$$\begin{cases} f(\bar{r}) = \frac{1}{(2\pi)^3} \int_{\mathbb{R}^3} F(\bar{\omega}) e^{i \bar{\omega} \cdot \bar{r}} d\bar{\omega} & (3DIFT) \end{cases}$$

So, I define $\bar{\omega} = \frac{\bar{g}}{KT} \Rightarrow \bar{g} = KT \bar{\omega}$:

$$\frac{Z_f(-iKT\bar{\omega}, T)}{(2\pi\omega KT)^{3/2}} = \int_{\mathbb{R}^3} Z_r(\bar{F}, T) e^{-i \bar{\omega} \cdot \bar{F}} d\bar{F}$$

Then:

$$Z_r(\bar{F}, T) = \frac{1}{(2\pi)^3} \int_{\mathbb{R}^3} \frac{Z_f(-iKT\bar{\omega}, T)}{(2\pi\omega KT)^{3/2}} e^{i \bar{\omega} \cdot \bar{F}} d\bar{\omega}$$

we define $\bar{\eta} = -KT \bar{\omega} \rightarrow d\bar{\eta} = (KT)^3 d\bar{\omega}$

$$Z_r(\bar{F}, T) = \frac{1}{(2\pi)^3} \int_{\mathbb{R}^3} \frac{Z_f(i\bar{\eta}, T)}{(2\pi\omega KT)^{3/2}} e^{-i \frac{\bar{\eta} \cdot \bar{F}}{KT}} \frac{d\bar{\eta}}{(KT)^3}$$

Since

$$\begin{aligned}
& (2\pi)^3 (2\pi\mu kT)^{3/2} (kT)^3 = \\
& = \left[2\pi kT \sqrt{2\pi\mu kT} \right]^3 = \\
& = \left[(2\pi kT)^{3/2} \sqrt{\mu} \right]^3 = (2\pi kT)^{9/2} \mu^{3/2}
\end{aligned}$$

We have:

$$\boxed{Z_T(\vec{F}, T) = \frac{1}{(2\pi kT)^{9/2} \mu^{3/2}} \int_{\mathbb{R}^3} Z_p(\vec{\eta}, T) e^{-i \frac{\vec{\eta} \cdot \vec{F}}{kT}} d\vec{\eta}} \quad [69]$$

2) Method based on the Laplace Transform theory:

In Eq. (68) we let $\vec{F} = -kT\vec{S}$ where \vec{S} is the vector Laplace variable:

$$Z_p(-kT\vec{S}, T) = (2\pi\mu kT)^{3/2} \int_{\mathbb{R}^3} Z_T(\vec{F}, T) e^{-\vec{S} \cdot \vec{F}} d\vec{F}$$

or, equivalently

$$\frac{\mathcal{Z}_f(-kT \bar{S}, T)}{(2\pi kT)^{3/2}} = \int_{\mathbb{R}^3} \mathcal{Z}_t(\bar{F}, T) e^{-\bar{S} \cdot \bar{F}} d\bar{F}$$

Now, we use the Laplace transform property:

$$F(s) = \int_{-\infty}^{+\infty} f(t) e^{-st} dt \quad (\text{LT})$$

$$f(t) = \frac{1}{2\pi i} \int_{\delta-i\infty}^{\delta+i\infty} F(s) e^{st} ds \quad (\text{ILT})$$

In three-dimensions

$$F(\bar{S}) = \int_{\mathbb{R}^3} f(\bar{F}) e^{-\bar{S} \cdot \bar{F}} d\bar{F} \quad (\text{3DLT})$$

$$f(\bar{F}) = \frac{1}{(2\pi i)^3} \int_{i\mathbb{R}^3} F(\bar{S}) e^{\bar{S} \cdot \bar{F}} d\bar{S} \quad (\text{3DILT})$$

Therefore:

$$\mathcal{Z}_r(\bar{F}, T) = \frac{1}{(2\pi i)^3} \int_{i\mathbb{R}^3} \frac{\mathcal{Z}_f(-kT \bar{S}, T)}{(2\pi kT)^{3/2}} e^{\bar{S} \cdot \bar{F}} d\bar{S}$$

Now, we change \bar{S} to \bar{a} through $\bar{S} = -i \frac{\bar{a}}{kT}$

→ $d\bar{S} = \left(-\frac{i}{KT}\right)^3 d\bar{\eta}$ and we obtain again

(33)

Z_F [69]:

$$\boxed{Z_F(F, T) = \frac{1}{(2\pi KT)^{3/2} \omega^{3/2}} \int_{\mathbb{R}^3} Z_f(i\bar{\eta}, T) e^{-i \frac{\bar{\eta} \cdot \bar{F}}{KT}} d\bar{\eta}} \quad [69]$$

Comments on the thermodynamic limit

In the scheme of prop 27 we have followed two different paths to obtain the thermodynamic description of a system. The two approaches lead to the same constitutive equation of the system under consideration only if the system is large enough. In this case we are in the thermodynamic limit.

The two equations $\bar{f} = \frac{\partial F}{\partial F}(\bar{F}, T)$ (for the Helmholtz ensemble) and $\bar{F} = -\frac{\partial G}{\partial f}(\bar{f}, T)$ (for the Gibbs ensemble) represent the same system if they are reciprocally inverse.

It happens if F and G are the Legendre transform of the other function. (34)

In other words, $\bar{f} = \frac{\partial F}{\partial f}$ is equivalent to

$$\bar{F} = -\frac{\partial G}{\partial \bar{f}} \text{ only if } G = F - \bar{f} \cdot \bar{F}.$$

In fact, by defining $\bar{F} = \phi(\bar{f})$ and $\bar{f} = \phi^{-1}(\bar{F})$ we obtain:

$$\begin{aligned} \frac{\partial G}{\partial \bar{f}} &= \frac{\partial F(\phi(\bar{f}), \tau)}{\partial \bar{f}} - \frac{\partial}{\partial \bar{f}} (\bar{f} \cdot \phi(\bar{f})) = \\ &= \frac{\partial \bar{F}}{\partial \bar{f}} \frac{\partial \phi}{\partial \bar{f}} - \phi(\bar{f}) - \bar{f} \frac{\partial \phi}{\partial \bar{f}} = \\ &= \bar{f} \frac{\partial \phi}{\partial \bar{f}} - \bar{f} \frac{\partial \phi}{\partial \bar{f}} - \bar{F} = -\bar{F} \end{aligned}$$

on the other hand

$$\begin{aligned} \frac{\partial F}{\partial \bar{F}} &= \frac{\partial G(\phi^{-1}(\bar{F}), \tau)}{\partial \bar{F}} + \frac{\partial}{\partial \bar{F}} (\phi^{-1}(\bar{F}) \cdot \bar{F}) = \\ &= \frac{\partial G}{\partial \bar{f}} \frac{\partial \phi^{-1}}{\partial \bar{F}} + \phi^{-1}(\bar{F}) + \bar{F} \frac{\partial \phi^{-1}(\bar{F})}{\partial \bar{F}} \\ &= -\bar{F} \frac{\partial \phi^{-1}}{\partial \bar{F}} + \bar{F} \frac{\partial \phi^{-1}(\bar{F})}{\partial \bar{F}} + \bar{f} = \bar{f} \end{aligned}$$

$G = F - \bar{P} \cdot \bar{F}$ is called the Legendre transform of F ; $F = G + \bar{P} \cdot \bar{F}$ is called the Legendre transform of G .

We have to show that F and G are reciprocally Legendre transformed under the thermodynamic limit.

To do this we observe the relations among the free energies and the partition functions

$$\boxed{\frac{\Delta}{Z_r} = e^{\frac{F}{kT}}} \quad \text{and} \quad \boxed{\frac{\Delta}{Z_f} = e^{\frac{G}{kT}}} \quad [70]$$

(they are derived from Eqs [47] and [46])

In the previous section we have obtained a relation between Z_r and Z_f in the form,

$$Z_f(\bar{P}, T) = (2\pi m k T)^{3/2} \int_{R^3} Z_r(\bar{F}, T) e^{-\frac{\bar{P} \cdot \bar{F}}{kT}} d\bar{F}$$

(see Eq. (68)) and therefore we may

Search for the relation between F and G (26)

$$e^{-\frac{G(\bar{F}, T)}{kT}} = (2\pi mkT)^{3/2} \int_{\mathbb{R}^3} e^{-\frac{F(\bar{F}', T)}{kT}} e^{\frac{\bar{F} \cdot \bar{F}'}{kT}} d\bar{F}'$$

now,

$$F(\bar{F}', T) = F(\bar{F}, T) + \frac{\partial F}{\partial \bar{F}} (\bar{F}' - \bar{F}) + \frac{1}{2} (\bar{F}' - \bar{F}) \cdot \frac{\partial^2 F}{\partial \bar{F}^2} (\bar{F}' - \bar{F})$$

and we let $\bar{F} = -\frac{\partial F}{\partial \bar{F}}(\bar{r}, T)$ and the inverse $\bar{F} = \bar{F}(\bar{r})$:

$$e^{-\frac{G}{kT}} = (2\pi mkT)^{3/2} \int_{\mathbb{R}^3} \exp \left[-\frac{F(\bar{F}, T)}{kT} - \frac{\bar{F} \cdot \bar{F}'}{kT} + \frac{\bar{F} \cdot \bar{F}}{kT} + \right. \\ \left. - \frac{1}{2kT} (\bar{F}' - \bar{F}) \frac{\partial^2 F}{\partial \bar{F}^2} (\bar{F}' - \bar{F}) + \frac{\bar{F} \cdot \bar{F}'}{kT} \right] d\bar{F}'$$

$$e^{-\frac{G}{kT}} = e^{-\frac{F - \bar{F} \cdot \bar{F}}{kT}} \cdot (2\pi mkT)^{3/2} \int_{\mathbb{R}^3} e^{-\frac{1}{2kT} (\bar{F}' - \bar{F}) \frac{\partial^2 F}{\partial \bar{F}^2} (\bar{F}' - \bar{F})} d\bar{F}'$$

$$-\frac{G}{kT} = -\frac{F - \bar{F} \cdot \bar{F}}{kT} + \ln \left\{ (2\pi mkT)^{3/2} \int_{\mathbb{R}^3} e^{-\frac{1}{2kT} (\bar{F}' - \bar{F}) \frac{\partial^2 F}{\partial \bar{F}^2} (\bar{F}' - \bar{F})} d\bar{F}' \right\}$$

$$G = F - \bar{F} \cdot \bar{F} - kT \ln \{ - \} \quad (27)$$

For a large system G, \bar{F} and $\bar{f} \cdot \bar{F}$ assume an extensive character and the \log term becomes negligible.

This is an heuristic proof of the thermodynamic limit.

Note on the partition functions with spherical symmetry

We suppose now that the partition function $Z_f(\bar{f}, T)$ depends on \bar{f} only through its modulus f

$Z_f(\bar{f}, T) = F(f, T)$ - We obtain

$$\begin{aligned}
Z_f(i\bar{\eta}, T) &= F(|i\bar{\eta}|, T) = \\
&= F(\sqrt{(i\bar{\eta})(i\bar{\eta})}, T) = F(i\sqrt{\bar{\eta} \cdot \bar{\eta}}, T) = \\
&= F(i\eta, T)
\end{aligned}$$

where η is the modulus of $\bar{\eta}$.

Therefore, Eq. [69] assumes the form:

$$Z_T(\bar{F}, T) = \frac{1}{(2\pi kT)^{3/2} \mu^{3/2}} \int_{R^3} Z_f(i\bar{\eta}, T) e^{-i \frac{\bar{\eta} \cdot \bar{F}}{kT}} d\bar{\eta} =$$

$$= \frac{1}{(2\pi kT)^{3/2} m^{3/2}} \int_{R^3} F(i\eta, T) e^{-\frac{i\eta \cdot \bar{F}}{kT}} d\eta \quad [72]$$

Now, $Z_T(\bar{F}, T)$ shows the spherical symmetry as well and thus $Z_T(\bar{F}, T) = R(r, T)$ when r is the modulus of \bar{F} .

In Eq. (72) we can assume $\bar{F} = r\bar{e}_z$ for simplicity; then:

$$R(r, T) = \frac{1}{(2\pi kT)^{3/2} \mu^{3/2}} \int_{R^3} F(i\eta, T) e^{-\frac{i\eta \cdot \bar{e}_z \cdot r}{kT}} d\eta \quad [73]$$

In spherical coordinates

$$\begin{aligned} \eta_x &= \bar{\eta} \cdot \bar{e}_x = \eta \cos\phi \sin\theta \\ \eta_y &= \bar{\eta} \cdot \bar{e}_y = \eta \sin\phi \sin\theta \\ \eta_z &= \bar{\eta} \cdot \bar{e}_z = \eta \cos\theta \end{aligned} \quad [74]$$

with Jacobian $J = \eta^2 \sin\theta$.

Therefore:

(39)

$$R(r, T) = \frac{1}{(2\pi kT)^{3/2} \omega^{3/2}} \int_0^{\infty} \int_0^{2\pi} \int_0^{\pi} F(i\eta, T) e^{-\frac{i\eta r \cos\theta}{kT}} d\theta d\psi d\eta \eta^2 \sin\theta$$

$$= \frac{2\pi}{(2\pi kT)^{3/2} \omega^{3/2}} \int_0^{\infty} \int_0^{\pi} F(i\eta, T) e^{-\frac{i\eta r \cos\theta}{kT}} \eta^2 \sin\theta d\theta d\eta$$

but

$$\int_0^{\pi} e^{-\frac{i\eta r \cos\theta}{kT}} \sin\theta d\theta$$

can be developed by means of the substitution $z = \cos\theta \rightarrow -\sin\theta d\theta = dz$
 $\rightarrow \sin\theta d\theta = -dz$

$$\int_0^{\pi} e^{-\frac{i\eta r \cos\theta}{kT}} \sin\theta d\theta = \int_{+1}^{-1} e^{-\frac{i\eta r z}{kT}} (-dz) =$$

$$= \int_{-1}^{+1} e^{-i \frac{\eta r z}{kT}} dz = \frac{kT}{-i\eta r} e^{-i \frac{\eta r z}{kT}} \Big|_{-1}^{+1} =$$

$$= \frac{kT}{-i\eta r} \left(e^{-i \frac{\eta r}{kT}} - e^{+i \frac{\eta r}{kT}} \right) = \frac{2kT}{\eta r} \operatorname{Sim} \frac{\eta r}{kT}$$

Finally:

$$R(r, T) = \frac{2\pi}{(2\pi kT)^{3/2} \mu^{3/2}} \int_0^{\infty} F(i\eta, T) \eta^2 \frac{2kT}{\eta r} \sin \frac{\eta r}{kT} d\eta =$$

$$= \frac{2}{(2\pi kT)^{3/2} \mu^{3/2}} \int_0^{\infty} F(i\eta, T) \frac{\eta}{r} \sin \frac{\eta r}{kT} d\eta$$

If $F(i\eta, T)$ is even in η i.e. $F(i\eta) = F(-i\eta)$ we obtain:

$$R(r, T) = \frac{1}{(2\pi kT)^{3/2} \mu^{3/2}} \int_{-\infty}^{\infty} F(i\eta, T) \frac{\eta}{r} \sin \frac{\eta r}{kT} d\eta$$

This is the relation among the partition functions $Z_f(\bar{f}, T) = F(f, T)$ and $Z_r(\bar{r}, T) = R(r, T)$ when they exhibit the spherical symmetry in their arguments.