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# "THERMODYNAMICS OF STRONG INTERACTIONS"

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# 3. THE MAIN PRINCIPLES OF STATISTICAL THERMODYNAMICS IN A NUTSHELL

## 3.1 The statistical ensemble of Gibbs (canonical ensemble)

The technique employed in hadron thermodynamics is that of the Gibbs canonical ensemble. If one renounces on all mathematical rigour, the main ideas can be formulated in a few lines of elementary algebra. This shall be done here just as a repetition of what we once have learned in a course on thermodynamics. For further reading, I recommend the marvellously short book (100 pages!) by Erwin Schrödinger (Schrödinger 1946), which is a real piece of art. The following discussion has been inspired by this book.

Let M be the macroscopic physical system which we wish to describe by statistical thermodynamics (in our context a piece of excited hadronic matter will be considered as macroscopic). Imagine now a number $N \to \infty$ of such systems, all equal to M. As macroscopic systems they are, however, not so equal to each other that they could not be distinguished; therefore we shall label them $M_1$, $M_2$ ... $M_i$... The Gibbs canonical ensemble is the the whole ensemble of them, packed together and in mutual thermic contact, but as a whole isolated from the rest of the world. The thermic contact may be arbitrarily small: such that the energy levels of the individual systems are barely changed.

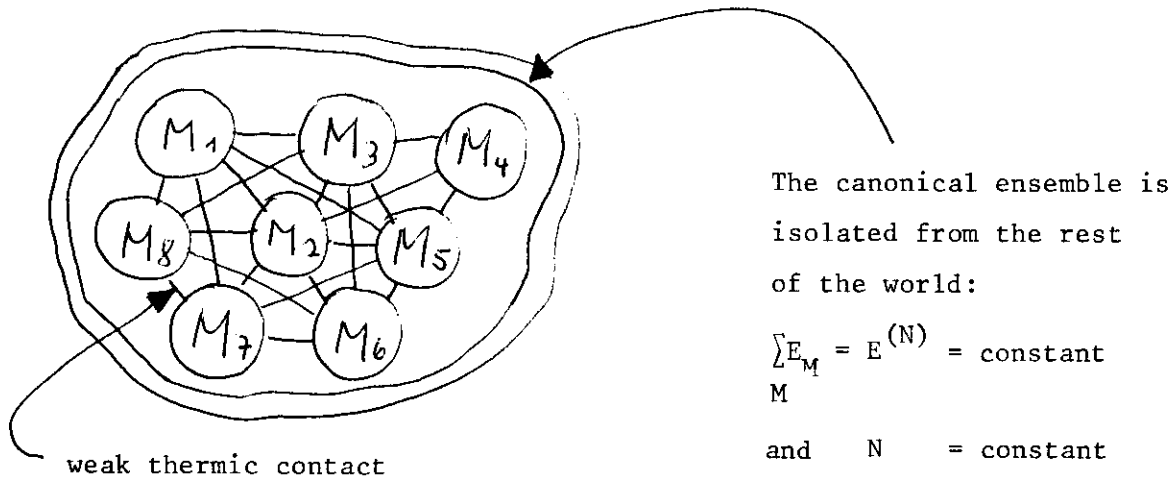


Fig. 4 A Gibbs canonical ensemble

The individual systems M have energy levels $E_1$, $E_2$ ... $E_i$... which are the same for each M, because the M's are equal. Suppose each M has a frontplate with a little screen showing a number i that indicates on which energy level $E_i$ this system actually is. Because of the thermic contact, each M frequently changes from one level i to another k, wandering thus through the whole level spectrum. Certain levels will be occupied more often than others; the most frequently occupied levels lie closely together and constitute the average energy of M. We shall now see how the M's are distributed over the level spectrum.

## 3.2 The distribution of the ensemble

Suppose we read off at given times $t_0$, $t_1$, etc. the state of our ensemble by recording the numbers i shown on the front plates. We sort them into a histogram :

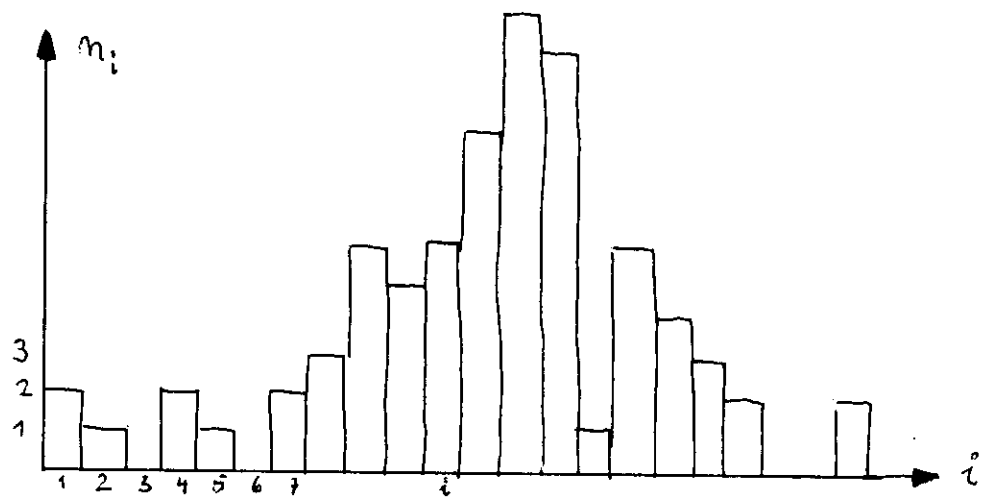


Fig. 5 An instantaneous state of the ensemble; at this moment six systems are found to be on level $E_i$, none on $E_3$, etc.

This histogram can equally well be represented by a point in an infinite dimensional space $R_\infty$:

$$\vec{n} = (n_1, n_2, n_3, \ldots n_i, \ldots) \qquad (3.1)$$

whose components $n_i$ count the number of systems occupying level $E_i$. Evidently

$$\sum n_i = N$$
$$\sum n_i E_i = E^{(N)} \tag{3.2}$$

To each vector $\vec{n}$ corresponds a distribution of our N systems over the energy level spectrum of M (not over the spectrum of the ensemble!). Suppose we record such instantaneous states, that is: such vectors $\vec{n}$, million and million times. The vectors will then show a distribution in $R_\infty$ which is densely centred somewhere, while the rest of $R_\infty$ is essentially unpopulated. Why? Because a distribution $\vec{n}$ can be achieved in many different ways:

$$P(\vec{n}) = \frac{N!}{n_1!\, n_2! \ldots n_i! \ldots} \tag{3.3}$$

is the number of possible realizations of $\vec{n}$. The density of points $\vec{n}$ in $R_\infty$ will be proportional to $P(\vec{n})$ and therefore be maximal around the vector

$$\vec{n}_{max} = (\bar{n}_1, \bar{n}_2, \bar{n}_3, \ldots \bar{n}_i, \ldots) \tag{3.4}$$

for which $P(\vec{n})$ = maximum. It can be shown that for $N \to \infty$, this maximum is extremely sharp and that all the rest can be neglected: almost all $\vec{n}$ fall together with $\vec{n}_{max}$.

We calculate the maximum logarithm of $P(\vec{n})$ with the supplementary conditions (3.2). We add these conditions multiplied by Lagrange parameters $\alpha$ and $\beta$, and find then the unconditional extremum (it will be a maximum) of

$$\ln P(\vec{n}) - \alpha \sum n_i - \beta \sum n_i E_i \tag{3.5}$$

which is given by

$$\frac{\partial}{\partial n_j}\left[-\sum_i \ln(n_i!) - \alpha\sum_i n_i - \beta\sum_i n_i E_i\right]_{n_i=\bar{n}_i} = 0 \qquad (3.6)$$

Hence

$$-\frac{\partial}{\partial n_j}\ln(n_j!) - \alpha - \beta E_j \Big|_{n_j=\bar{n}_j} = 0 \qquad (3.7)$$

Remember now Stirling's formula

$$\ln(k!) = \ln 1 + \ln 2 + \ldots + \ln k \approx \int_1^k \ln x\, dx$$

so that

$$\frac{d}{dk}\ln(k!) \approx \ln k \qquad (\text{for } k \to \infty) \qquad (3.8)$$

Now, since $N \to \infty$, each $n_i \to \infty$; hence we can use (3.8) without remords. Then (3.7) gives

$$\ln \bar{n}_j = -\alpha - \beta E_j \qquad \text{or} \qquad \bar{n}_j = e^{-\alpha-\beta E_j} \qquad (3.9)$$

where $\alpha$ and $\beta$ have to be determined such that the supplementary conditions (3.2) are fulfilled

$$\sum_i n_i = e^{-\alpha}\sum_i e^{-\beta E_i} = N \quad (\Rightarrow \infty) \qquad (3.10)$$

$$\sum_i n_i E_i = e^{-\alpha}\sum_i E_i e^{-\beta E_i} = E^{(N)} \quad (\Rightarrow \infty)$$

If the level spectrum $\{E_1, E_2, \ldots E_i \ldots\}$ is known, then $\alpha$ and $\beta$ can be calculated by solving eq. (3.10). But we need not even do this, because we can at once eliminate $\alpha$ by dividing the second equation by the first, obtaining thus the average energy $\bar{E}$ of our system:

$$\frac{E^{(N)}}{N} \equiv \bar{E} = \frac{\sum E_i e^{-\beta E_i}}{\sum e^{-\beta E_i}} \equiv -\frac{d}{d\beta}\left[\ln \sum e^{-\beta E_i}\right] \qquad (3.11)$$

Furthermore; select randomly a system M from the ensemble; the probability to find it on the level $E_j$ is given by equations (3.9) and (3.10):

$$\frac{\bar{n}_j}{N} \equiv w_j = \frac{e^{-\beta E_j}}{\sum e^{-\beta E_i}} \equiv -\frac{1}{\beta}\frac{\partial}{\partial E_j}\left[\ln \sum e^{-\beta E_i}\right] \qquad (3.12)$$

Again, the parameter $\alpha$ has disappeared and we shall see that indeed we need not worry about $\alpha$, nor about $\beta$; we shall find out the physical significance of $\beta$ in a moment.

Before we do that, let me stress the central importance of the quantity $\sum e^{-\beta E_i}$. It is so important, that it has its own name:

$$Z(V, T) \equiv \sum_i e^{-\beta E_i} = \begin{matrix}\text{"partition function"} \\ \text{or "sum over states"}\end{matrix} \qquad (3.13)$$

The variable V indicates that the level spectrum of the system depends on its volume, and T anticipates that $\beta$ will turn out to be the inverse of the temperature.

The importance of Z(V, T) lies in the fact, that the most probable distribution $\vec{n}_{max} = (\bar{n}_1, \bar{n}_2, \ldots \bar{n}_j \ldots)$ is obtained as the logarithmic derivative of Z with respect to the $E_j$, and that together with this distribution all expectation values of all interesting quantities are also calculable from Z(V, T), as for instance the mean energy $\bar{E}$ [eq. (3.11)]. Thus one can say without exaggerating:

the central task of statistical thermodynamics is to calculate the partition function

$$Z(V,T) = \sum_i e^{-\beta E_i}$$

which implies the knowledge of the level spectrum.

## 3.3 Relation of statistics to thermodynamics

We now link these statistical considerations to thermodynamics. In thermodynamics we consider a system (just one of our $N = \infty$), and ascribe to it energy, temperature, entropy, volume, pressure, and so on. If we speak of temperature T, then we imagine our system coupled to a thermostat or embedded in a heat bath of temperature T. Being in thermic contact with a heat bath, its energy content is not exactly sharp, but fluctuates very little around some mean value $\bar{E}$, relative fluctuations are smaller, the larger our system is.

The first law of thermodynamics states

$$d\bar{E} = T\,dS - P\,dV \tag{3.14}$$

We introduce the "free energy" F by

$$F \equiv \bar{E} - TS \tag{3.15}$$

Hence

$$dF = d\bar{E} - T\,dS - S\,dT = -S\,dT - P\,dV \tag{3.16}$$

While the "natural variables" of $\bar{E}$ are S and V -- namely the ones of which $d\bar{E}$ is a complete differential -- the natural variables of F are seen to be T and V.

We find then, among other relations of this sort, that

$$S = -\left(\frac{\partial F}{\partial T}\right)_V \tag{3.17}$$

Inserting this into (3.15) yields

$$\bar{E} = F + TS = F - T\frac{\partial F}{\partial T} = T^2\frac{\partial}{\partial T}\left[-\frac{F}{T}\right] \equiv -\frac{\partial}{\partial(\frac{1}{T})}\left[-\frac{F}{T}\right] \tag{3.18}$$

This can be compared to the corresponding formula in the statistical description [(3.11) and (3.13)] :

$$\bar{E} = -\frac{\partial}{\partial\beta}\left[\ln Z(V,T)\right] \tag{3.19}$$

This is the average energy of a system, which as a member of an ensemble of N = $\infty$ such systems, is in weak contact with them -- in other words: the N - 1 remaining systems of the Gibbs canonical ensemble play the role of a heat bath for the one system considered. Thus identifying eqs. (3.18) and (3.19) we read off:

$$\bar{E} = -\frac{\partial}{\partial(\frac{1}{T})}\left[F(V,T)/T\right] = -\frac{\partial}{\partial\beta}\left[\ln Z(V,T)\right]$$

So that we can identify

$$\beta = \frac{1}{T}$$

$$\ln Z = -\frac{F}{T} + G(V) \tag{3.20}$$

Where G is still an arbitrary function of V. We determine this function by comparing the partial derivatives with respect to V. We find

$$\frac{\partial}{\partial V} \ln Z = \frac{-\frac{1}{T}\sum \left(\frac{\partial E_i}{\partial V}\right) e^{-\frac{E_i}{T}}}{\sum e^{-\frac{E_i}{T}}} \equiv -\frac{1}{T}\overline{\left(\frac{\partial E_i}{\partial V}\right)} \tag{3.21}$$

Thus

$$\frac{\partial}{\partial V}\left[-T \ln Z(V,T)\right] dV = \overline{\left(\frac{\partial E_i}{\partial V}\right)} dV \tag{3.22}$$

This is the total change of the energy of M, brought about by the small shifts of all individual levels $E_i$, when the volume V is changed by dV, in other words: it is the external work - PdV done by the system when V is increased by dV; thus, with (3.20)

$$\frac{\partial}{\partial V}\left[-T \ln Z\right] = -P = \frac{\partial F}{\partial V} - T\frac{\partial G}{\partial V} \tag{3.23}$$

On the other hand, from (3.16)

$$\frac{\partial F}{\partial V} = -P \tag{3.24}$$

so that G(V) can at most be a constant, since $\partial G/\partial V$ must vanish. Such a constant is of no interest, because the free energy is anyway only defined up to a constant. Therefore, we have finally

$$\beta = \frac{1}{T}$$

$$\ln Z(V,T) = -\frac{F(V,T)}{T}$$

$$\bar{E} = T^2 \frac{\partial}{\partial T}\left[\ln Z(V,T)\right] \qquad (3.25)$$

$$P = T \frac{\partial}{\partial V}\left[\ln Z(V,T)\right]$$

$$w_j = -T \frac{\partial}{\partial E_j}\left[\ln Z(V,T)\right]$$

In this notation the Lagrange parameter $\beta$ has obtained the physical significance of the inverse temperature and the relation to thermodynamics is fully established. P and $\bar{E}$ appear in a parametric representation which may be rewritten, by eliminating either T or V, as

$$P = f(\bar{E}, V) = g(T, V) = h(\bar{E}, T) \qquad (3.26)$$

which is the equation of state of our system. Hence literally everything is calculable from Z(V, T).

## 3.4 The importance of the level density $\sigma(E, V)$

Let us illustrate these results. A macroscopic system has "continuous energy"; that is to say, its energy levels lie extremely dense. Therefore, we write

$$Z(V,T) = \sum_i e^{-\frac{E_i}{T}} = \int_0^\infty \sigma(E,V)\, e^{-\frac{E}{T}}\, dE \qquad (3.27)$$

with $\sigma(E, V)dE$ = number of energy levels in $\{E, dE\}$.

We see here that for calculating $Z(V, T)$, we do not need to know the levels $E_1, E_2, \ldots E_i$ individually; if they lie close enough, their density $\sigma(E, V)$ suffices to calculate $Z(V, T)$:

$Z(V, T)$ and $\sigma(E, T)$
are Laplace transforms of each other and the knowledge of one implies that of the other.

What can we conclude about $\sigma(E, V)$ from our daily-life knowledge about thermodynamic systems?

- The energy of a macroscopic body is "continuous", hence $\sigma(E, V)$ is "large" (in some sense or other);
- The energy of a macroscopic body is "sharp"; this means that $\sigma(E, V)$ is fast increasing with E. This can be seen as follows: Eq. (3.25) says

$$\bar{E} = T^2 \frac{\partial}{\partial T} \left[ \ln \int \sigma(E, V) e^{-E/T} dE \right]$$

$$= \frac{\int E \sigma(E, V) e^{-E/T} dE}{\int \sigma(E, V) e^{-E/T} dE} \tag{3.28}$$

Thus, $\bar{E}$ is the meanvalue of E with respect to the distribution function $\sigma(E, V)\ e^{-E/T}$ which, for sharp $\bar{E}$, must have a sharp maximum at $E = \bar{E}$. This is the case when $\sigma(E, V)$ is a rapidly increasing function of E, which indeed it is, as we remember from the textbooks.

If $\sigma(E, V)\ e^{-E/T}$ has a sharp maximum at $E \cong \bar{E}$, then with some $\Delta E$ around $\bar{E}$

$$Z(V, T) \approx \sigma(\bar{E}, V) e^{-\frac{\bar{E}}{T}} \Delta E \tag{3.29}$$

Then indeed, we obtain back from (3.25)

$$\bar{E} = T^2 \frac{\partial}{\partial T}[\ln Z] = T^2 \frac{\partial}{\partial T}\left[\ln \sigma(\bar{E},V) - \frac{\bar{E}}{T} + \ln \Delta E\right] = \bar{E}$$

as we should; but furthermore, we find with (3.17) for the entropy

$$S(\bar{E},V) \equiv -\frac{\partial F}{\partial T} = \frac{\partial}{\partial T}[T \ln Z] = \ln Z + T \frac{\partial}{\partial T}[\ln Z]$$

$$= \ln \sigma(\bar{E},V) - \cancel{\frac{\bar{E}}{T}} + \ln \Delta E + \cancel{\frac{\bar{E}}{T}} \simeq \ln \sigma(\bar{E},V) \qquad (3.30)$$

Neglecting the unimportant ln $\Delta E$, we thus obtain the key relation

$$\ln \sigma(\bar{E},V) = S(\bar{E},V) \qquad (3.31)$$

which once more illustrates the central role played by the level density $\sigma(E, V)$. We learn still another important lesson by comparing eqs. (3.27) and (3.31)

> $Z = \int \sigma(E, V)\, e^{-E/T} dE$ has tought us that the detailed level spectrum $\{E_1, E_2, \ldots E_i \ldots\}$ need not be known and that the knowledge of $\sigma(E, V)$ suffices to calculate everything; now from $\ln \sigma(E, V) \cong S(E, V)$, we see that the thermodynamically (macroscopically) relevant quantity is not even $\sigma(E, V)$ but its logarithm.

This last remark seems perhaps senseless, because mathematically f(x) and ln f(x) contain exactly the same information. Mathematically, yes, but not physically in a thermodynamical sense:

two systems with level densities $\sigma_1(E, V)$ and $\sigma_2(E, V)$ become thermodynamically equivalent for $\overline{E} \to \infty$ , when

$$\lim_{E\to\infty} \frac{\ln \sigma_1(E,V)}{\ln \sigma_2(E,V)} = 1$$

no matter to what limit $\sigma_1/\sigma_2$ or $\sigma_1 - \sigma_2$ tend.

Example: for an ideal gas of N particles, we have [see (3.34) and (3.35a)]

$$\sigma_N(E,V) = \frac{1}{E} \cdot \left(e\frac{V}{N}\right)^N \cdot \left(\frac{mE}{3\pi N}\right)^{\frac{3N}{2}}$$

Thus, comparing two gases with $N_1$ and $N_2 = N_1 - n$ particles respectively, we have for $T \to \infty$ and $n << N_1$

$$\frac{\sigma_{N_1}(E,V)}{\sigma_{N_2}(E,V)} \cong \left(e\frac{V}{N}\right)^n \cdot \left(\frac{mE}{3\pi N}\right)^{\frac{3n}{2}} \quad \nearrow \infty \text{ for } E\to\infty,\ N \text{ fixed} \qquad \searrow 0 \text{ for } N\to\infty,\ E \text{ fixed}$$

$$\frac{\ln \sigma_{N_1}(E,V)}{\ln \sigma_{N_2}(E,V)} \cong 1 + \frac{n}{N_1}$$

In other words: if from a macroscopic gas, I remove a few molecules, then the level density becomes, for $E \to \infty$, infinitely different from what it was before, but the thermodynamics is not changed at all.

The thermodynamic equivalence of two systems will logarithmically equal level densities (i.e. equal entropies) will be used in our treatment of strong interactions; a first application will be seen now.