7. Statistics and quantum molecular issues

Preceding chapters have addressed the study of quantum states sutained by material systems taken. The role played by I-frames is central as it is the resource used to locate systems in laboratory space; it provides also with the origin to construct a configuration space where (internal) quantum states are projected; namely, an abstract mathematical space that remains that way unless couplings with external potentials (systems) are incorporated in specific theoretic schemes at the Fence.

We used Feynman's quantum mechanics in real space settings. The relation between material systems in laboratory space and quantum state defined in abstract spaces goes through material parameters (mass, charge) entering the eigenvalue equations that generates bases states and eigenvalues of operators related to physical properties: Hamiltonian, angular momenta. The place occupied by classical particles is taken over by the I-frame concept and the paths are just a pictorial way to describe the evaluation of an integral.

In so far quantum aspects are concerned nothing changes because one focus attention on the quantum states and not in the way the material system sustaining them behaves in a classical sense; couplings between these levels must be handled on a case by case basis. The game to master here is the construction of a passage from a set of N independent I-frame systems that we can partition in different aggregates. We study ways one may construct to distribute the N-systems in base states of a common container (Box).

From relativistic mechanics discussed in preceding chapters an I-frame system besides the total mass and charge is also identifiable by spin labels. In this chapter we keep as much as one can the emphasis on quantum states and present first a short review of statistical aspects to follow with the study of assemblies of bosons first and thereafter fermions. Because the states of a particle system is related to infinite number of base states one changes counting particles by the counting of states: density of states becomes a key magnitude. Here one moves from few I-frame systems to intermediate size condensates until getting at solid-state aspects. For the sake of completeness some of the simple models used to construct base sets are discussed again; this time emphasis is on the special characteristics shown by chemical physics systems.

7.1. N-copies of single systems: Gibbs ensemble

One of the factor missing so far is related to thermodynamic and the variables, volume (V), pressure (P) and absolute temperature (T) that are required for a proper characterization of material systems at a laboratory level. Define a given volume in laboratory space; take one I-frame system and calculate particle-state in a box, the procedure yields energy labels (levels) for a system the mass located at the origin of that I-frame; the internal quantum space (if any) is not touched. This trick permits introducing energy levels that are functions of the volume; the initial particle I-frame vanishes, this is a sort of quantization procedure. Each of the N-copies is assigned a particular label.

At the foundation of statistical mechanics lies the idea of well-defined objects. An object (molecule, atom) is characterized by a a particular label selected from a set of energy levels $\{\varepsilon_k\}$; the particle occupies one level and only one. How many particles can occupy a given level depends upon spin to be examined later on. To each energy value a base state $|\varepsilon_k>$ is assigned as well as an eigen function labeled by the ordinal number affecting the energy level (the set is denumerable). Yet one should not forget energy differences between eigenvalues are the actual physical quantities at a Fence. Actual energy exchange between subsystems occurs at a laboratory level; something like the "real world" but, because of the assumption of equilibrium one does not need to care for.

From thermodynamics we take the concept of thermal equilibrium at temperature T. In principle, there is an energy source/sink that would eventually lead to thermal equilibrium that is not included. We can then suspect that quantum states showing a variety of non-zero amplitudes will result after interactions with the thermal bath. Because at this stage one is not concerned with the mechanism leading to a thermal equilibrium but acknowledges $k_B T$ as the measure of "quantum" of thermal energy; k_B is Boltzmann constant.

If the single system shows no entanglement with the thermal bath as it should be the case one can define a quantum state as a linear superposition such as:

$$|\Psi, T> = \sum_k |\varepsilon_k><\varepsilon_k|\Psi,T> =$$

$$\sum_k |\varepsilon_k> C_k(\Psi,T) \qquad (7.1.1)$$

The label T plays the role of a kind of time; the Hamiltonian $\hat{H}$ characterizes the one-system.

Statistical thermodynamics revolves around the partition functions q defined as:

$$q = \Sigma_k \exp(-\varepsilon_k /k_B T) \qquad\qquad (7.1.2)$$

Calculating now the average value of the Hamiltonian with eq.(7.1.1) one gets:

$$E(T) = <\Psi, T| \hat{H} |\Psi, T> = \sum_k \varepsilon_k [C_k(\Psi,T)]^2 \quad (7.1.3)$$

A consistency requirement for thermal equilibrium leads to the assignment:

$$[C_k(\Psi,T)]^2 \ \alpha \ \exp(-\varepsilon_k /k_B T) / q \qquad\qquad (7.1.4)$$

It is a common assumption of standard quantum mechanics that for a molecular system, one molecule can be in one and only one of the accessible states; we retain this view for the time being to check how far one can go. In this perspective, a system of N *non-interacting* "molecules" is distributed among box states, and the number n_k of systems having energy ε_k in the collective of N systems in thermal equilibrium is given by:

$$n_k = N (1/q) \exp(-\varepsilon_k /k_B T) = N[C_k(\Psi,T)]^2 \qquad (7.1.5)$$

The second equality implies that N independent systems in the box; the number n_k is proportional to the amplitude square in agreement with a population model.

At this point note that total quantum state for the system in the box appears to be a simple product of individual quantum states for which the projection hypothesis holds.

Conservation of molecules number is then ensured due to normalization of the quantum state

$$N = \Sigma_k n_k = \Sigma_k N[C_k(\Psi,T)]^2 = N \Sigma_k \left| C_k(\Psi,T) \right|^2 \ (7.1.6)$$

For N non-interacting copies the average energy E_{av} reads:

$$E_{av} = N <e> = N (1/q) \Sigma_k \varepsilon_k \exp(-\varepsilon_k /k_B T) =$$

$$\Sigma_k n_k \varepsilon_k \qquad\qquad (7.1.7)$$

For the time being we take the energy levels as functions of the volume V: $\varepsilon_k(V)$. Thus, the average energy is a function of V,T and N: $E_{av}(V,T,N)$.

The quantity $[C_k(\Psi,T)]^2$ equals n_k /N may be seen in two different manners. It is a relative occupation of the k-th base state. Or we can use our point of view: it just indicates the relative intensity response from the root state ε_k when a probe targeted to the spectrum rooted on that level is used at the Fence. This latter interpretation avoids the necessity imposed by the particle model. For now one can actually think that the measurement of root state activations is modulated by the amplitude in modulus square of the quantum state given in eq.(7.1.1). A probe designed to sense the coherent linear superposition would never be measuring such incoherent quantities.

In general quantum mechanical terms, the average value of a hermitean operator $\hat{O}$ is given in the energy base set eq.(7.1.1) by:

$$<\hat{O}> = O_{av} =$$

$$\sum_k \sum_{k'} C_{k'}{}^*(\Psi,T) <\varepsilon_{k'}| \hat{O} |\varepsilon_k> C_k(\Psi,T) \qquad (7.1.8)$$

For a diagonal operator in this base set one has: $<\varepsilon_{k'}| \hat{O} |\varepsilon_k> = <\varepsilon_k| \hat{O} |\varepsilon_k> \delta_{k'k}$. Moreover, if the quantum state stands for a Gibbs ensemble then the quantum average turns out to be given as a statistical mechanical average:

$$<\hat{O}> = O_{av} = (1/q)\Sigma_{|\eta k>} <\varepsilon_k| \hat{O} |\varepsilon_k> \exp(-\varepsilon_k /k_B T) \qquad (7.1.9)$$

We can see that eq.(7.1.4) multiplied by the number of copies N tells us that $N|C_k(\Psi,T)|^2$ is just given by the canonical distribution: $N (1/q) \exp(-\varepsilon_k /k_B T)$. This result was also found in eq.(7.1.5) that yields the number of system in the ensemble associated to energy ε_k.

For ensembles where the copies are described by an arbitrary quantum state the canonical density matrix operator is given by:

$$\hat{\rho} = \exp(- \hat{H}/k_B T) \qquad (7.1.10)$$

The quantum average over a base set where the Hamiltonian is not diagonal is given by:

$$<\hat{\rho}>(t) = \sum_k \sum_{k'} C_{k'}{}^*(\Psi,t) C_k(\Psi,t) <\eta_{k'}| \hat{\rho} |\eta_k>$$
$$(7.1.11)$$

The evolution in time starting from $<\hat{\rho}>(t_o)$ is then controlled by the time evolution of the amplitudes different from zero that were prepared at initial time.

As we have discussed in previous chapters, if you take $\hat{H}$ from eq.(7.1.10) to be diagonal in the basis set used in eq.(7.1.11) there will be no real change in amplitudes. One stays in the formalism realm describing systems in thermal equilibrium.

7.2. Jaynes-Shannon model

So far the relationship between amplitudes and statistical distributions has followed an analogical path. Jaynes use of Shannon information theory formalism leading to a general formulation of statistical mechanics (Jaynes, E.T. Phys.Rev.106, 620-630) may give us a hand. The maximum entropy principle is the key to construct many sorts of statistical distributions.

Introduce now a set $\{f_k\}$ of *characteristic frequencies* to be related, at a later stage, to the occupation frequency N^k/N. A characteristic frequency is an intensive quantity defining the property of a system under specific experimental constraints.

One asserts existence of these characteristic frequencies. The function f_k is a positive number that can vary from zero to one; when the occupation number is zero, $f_k = 0$, there are no molecules in the k-th state. When $f_k = 1$, only the k-th state has an occupation number different from zero, all the molecules are in the k-th state. Alternative formulation: f_k is zero for all cases where the k-th state has zero occupancy; when f_k is equal to one the k-th state is the only one that is occupied. The difference is important whenever the photon field and excited states are involved; or spin selection rules must be respected, e.g. ortho/para hydrogen.

In normal systems, the energy levels should have assigned such quantities. The problem is to derive equations connecting these objects to experimentally measurable properties.

Shannon function approach. Introduce now a function of these characteristic frequencies, namely, the Shannon function $S\hbar = S\hbar(f_1, \ldots, f_k, \ldots)$. We take the dimensionless form:

$$S\hbar = -\Sigma_k f_k \ln f_k \qquad (7.2.1)$$

Because $0 \le f_k \le 1$, Shannon function $S\hbar$ is always positive; the natural logarithm of a quantity smaller or equal to one yields a negative value; for all f_k that are zero, the factor in front the logarithm kill the infinite terms. For example, a collection of N states not occupied, each term in the sum is zero, $S\hbar(\text{empty}) = 0$. Observe that the quantum mechanical representation of quantum states retained in the present work is perfectly adapted to such a treatment. As a matter of fact, people working in quantum information theory employ such a type of analysis.

For a system where all elements can occupy one and only one state, the Shannon function is zero also. Thus, if S is a well-behaved function between these two limits, then S must show a maximum.

Note that the set $\{f_k\}$ is a characteristic property of the state that a given system may have at a given time; the problem of statistical mechanics is to find out the distribution for a particular system under specific constraints that can be mapped out to these characteristic frequencies.

Microcanonical ensemble. This corresponds to an isolated system in equilibrium. The system energy ranges in the interval (E, E + δE); assume that there are W(E,V,N) different micro states with energy ε_k. Hence, the characteristic frequency f_k=1/ W(E,V,N) if ε_k lies in the interval (E, E + δE), then f_k=0 if the energy level lies outside the energy shell. Some counting models are discussed below.

In statistics, a concept of probability is used instead of our characteristic frequencies. Let $\mathcal{N}$ be the total number of microstates in the ensemble; and consider the number of times ν_j the j-th microstate is "sorted out" in a counting procedure or experimentally measured somehow. The probability (measured as a frequency) to pick the j-state out is then $p_j = (\nu_j /\mathcal{N})$. The average of A will be now eq.(7.2.2):

$$<\hat{O}> =(1/\mathcal{N})\Sigma_j <\varepsilon_j| \hat{O}|\varepsilon_j> \nu_j = \Sigma_j <\varepsilon_j| \hat{O}|\varepsilon_j> p_j \quad (7.2.2)$$

For the micro canonical ensemble you assume that a measurement time is so short that the system is considered to be in only one microstate; thus you collect them (count) and get ν_j. Finally, the ensemble average $<\hat{O}>$ is taken to represent the measured value O_{obs}. This picture is akin to the idea that each molecule occupies one and only one micro state.

Eq.(7.2.1) multiplied by Boltzmann constant (to keep dimensions correctly, $S_J = k_B S\hbar$) becomes the definition of Jaynes' entropy for the micro canonical ensemble:

$$S_J(E,V,N) = k_B \ln W(E,V,N) \quad\quad\quad (7.2.3)$$

It is interesting to introduce now statistical probabilities; these can be attained experimentally at variance with the characteristic frequencies. Let the ratio $(\mathcal{N}/N)$ represent the number of replicas ν of the N-particle-copies system; that is a huge number for macroscopic systems.

We assume that for each replica we have the same probability distribution $p_1, p_2, \ldots, p_k, \ldots$ of populating the micro state $1,2,\ldots,k,\ldots$ respectively. For a sufficiently large ν, the number of systems in the ensemble that are in the state r is given by

$$\nu_r = \nu \, p_r \qquad (7.2.4)$$

The statistical weight W_ν of the ensemble when n_1 of its systems are in state 1, n_2 of its systems in the state 2, … is the number of ways in which this particular distribution can be realized, i.e.

$$W_\nu = \nu! \, / \, \nu_1! \, \nu_2! \ldots \nu_r! \ldots \qquad (7.2.5)$$

The ensemble entropy is given by

$$S_\nu(\text{ensemble}) = k_B \ln W_\nu \qquad (8.2.6)$$

Replacing now the corresponding distribution function

$$S_\nu(\text{ensemble}) = k_B \ln (\nu! \, / \, \nu_1! \, \nu_2! \ldots \nu_r! \ldots) \qquad (7.\,2.7)$$

Stirling formulae helps calculating the factorials: $\ln(m!) = m \ln(m) - m$:

$$S_\nu(\text{ensemble}) = k_B (\nu \ln \nu - \Sigma_r \, \nu_r \ln \nu_r) \qquad (7.2.8)$$

Now, we have eq.(7.2.4) relating the number of systems in a given state to the probability of finding it there ($\nu_r = \nu \, p_r$). One finally obtains:

$$S_\nu(\text{ensemble}) = -k_B \, \nu \, (\, \Sigma_r \, p_r \ln p_r) \qquad (7.2.9)$$

The entropy of a single system (as the one we have been using) is given

$$S(\text{one-system}) = S_\nu(\text{ensemble})/ \, \nu =$$

$$-k_B (\Sigma_r \, p_r \ln p_r) \qquad (7.2.10)$$

The entropy obtained from the statistical probabilities has the same form than Shannon function. We can hence think of a map between the p_r and the f_rs. Thus, consistency between the entropy obtained by multiplying Shannon function by Boltzmann constant and eq.(7.2.11) requires that:

$$p_r \rightarrow f_r \qquad (7.2.11)$$

A successful statistical modeling will produce portraits of the intrinsic properties of the system. (See below and Jaynes (1980)).

It is important to realize the logical difference between these quantities. The p_r-frequencies (probabilities) represents actual results of measurements while f_r, the characteristic–frequency, is a property of the state of the system (including external constraints).

You wouldn't be surprised if we take the assignment above, i.e. $p_r \rightarrow f_r \rightarrow |C_r(\Psi,T)|^2$ and get the standard statistical interpretation of quantum mechanics! You also realize that coherence effects vanish. But, if you plan spectroscopic probing targeting specific root state so that coherence is not relevant, then one obtains relative response intensities $|C_r(\Psi,T)|^2$ depending on absolute

temperature. Temperature modulates the spectral response as it is well documented for the "hot-bands" in spectroscopy.

Start from the normalization condition and renaming the square amplitudes with symbol f_k:

$$\Sigma_k \ [C_k(\Psi,T)]^2 = \ \Sigma_k \ f_k = 1 \qquad\qquad (7.2.12)$$

This equation comes up as a result relating a quantum state for a material system put in thermal equilibrium with a bath at absolute temperature T. Shannon model implemented by Jaynes leads to establishing a rather natural connection between the quantum state of each replica with statistical distributions over states occupancies. Since the system is assumed to be in thermal equilibrium we do not need to care for mechanisms of energy exchange that would, at the laboratory, lead to such thermal state. The set $\{C_k(\Psi,T)\}$ is calculated with the canonical ensemble recipe eq.(7.1.4) to within a factor.

For a system that is not in equilibrium, the amplitudes are time dependent; irreversible process description can be made in this framework. If we take as model the example discussed in Chapter 1 one can easily figure out the effect of increasing temperature, namely, a chemical change. Quantum mechanics can give us clues on the quantum paths such a system may take. While statistical mechanics inform us on the set of amplitudes in square modulus that can be extracted from eq.(7.1.5).

In general, one can prepare system with arbitrary occupation numbers. The total number of occupied states being N that corresponds to the number of copies (Jaynes E.T. Ann.Rev. Phys. Chem. 31 (1980) 579-601). Call N^k an arbitrary assignment to the k-th state (of one copy if you prefer) with the constraint equivalent to eq. (7.2.2), namely,

$$N = \Sigma_k \ N^k \qquad\qquad (7.2.13)$$

The total energy differs from eq.(7.1.7) because the distribution now is not the equilibrium one:

$$E = \Sigma_k \ N^k \ \varepsilon_k \qquad\qquad (7.2.14)$$

It is apparent that we must focus on the sets of different $\{N^k\}$ satisfying eq.(7.2.2).

Canonical ensemble. All states with fixed (size) number N, and volume but the energy can fluctuate: <E>. This ensemble describes systems in contact with thermal baths.

To obtain the entropy of a system in a heat bath, substitute eq. (7.1.5) after giving it the form: $f_k = n_k/N = (1/q)\exp(-\varepsilon_k /k_B T)$, into eq.(7.2.1) multiplied by Boltzmann constant:

$$S(V,<E>,N) = k_B \ln q + <E>/T \qquad (7.2.15)$$

The question is whether such replacement is consistent or not.

Let us first show the correctness of the substitution made to get the entropy $S(V,<E>,N)$, namely the use of Boltzmann distribution. The problem is to find a distribution that renders Shannon function to a maximum under the constraints of energy and particle conservation. Average energy is given as:

$$E_{Av} = <E> = \Sigma_k f_k \varepsilon_k \qquad (7.2.16)$$

Employing Lagrange multipliers to mix variations δS, $\delta \Sigma_k f_k$ and $\delta(E_{Av})$ where the energy levels are invariant (constant volume), that is:

$$\delta S - \beta \delta(E_{Av}) - \lambda \delta \Sigma_k f_k = 0 \qquad (7.2.17)$$

The dimension of β is inverse energy, λ is dimensionless, one easily obtains:

$$f_k = \exp(-\beta\varepsilon_k - \lambda) \qquad (7.2.18)$$

The relationship $f_r \rightarrow |C_r(\Psi,T)|^2$ still holds true independently from the type of ensemble. Now, the parameter λ is given as:

$$\lambda = \ln (\Sigma_k \exp(-\beta\varepsilon_k)) = \ln q(\beta) \qquad (7.2.19)$$

For a system in thermal equilibrium $\beta=1/k_B T$ and $q(\beta)$ is just a partition function. In this case, by making the assignment $f_k \rightarrow n_k/N$, eq. (7.2.2) is immediately fulfilled. The initial model is hence recovered with the help of Shannon function. *The set of n_k /N renders Shannon function stationary (maximum) compatible with energy and particle number conservation.*

Formally we have found consistency. We will now use the construction starting from the micro canonical ensemble.

From the statistical point of view we have identified $W(<E>,V,N)$ to $W(E,V,N)$. The concept of ensemble permits solving this issue. For now $\nu\rightarrow\infty$ as well as the volume in such a way density is constant. This is the thermodynamic limit. In this case, the relative fluctuation in the average energy goes to zero. One can confidently replace $<E>$ by E and write $S(V,<E>,N) \rightarrow k_B \ln W(<E>,V,N) \rightarrow k_B \ln W(E,V,N) \rightarrow S(V,E,N)$. Consequently

$$S(V,E,N) = Nk_B \ln q + E/T \qquad (7.2.20)$$

Rearranging this,

$$E - TS = - N k_B T \ln q = - k_B T \ln q^N = - k_B T \ln Q$$

This is Helmholtz free energy $\mathcal{A}$, i.e. $E - TS = \mathcal{A} (V,T,N)$. This is just equal to the natural logarithm of the partition function $q(T,V,N)$ multiplied by minus $k_B T$. This is a fundamental result:

$$\mathcal{A}(V,T,N) = - k_B T \ln Q \qquad\qquad (7.2.21)$$

Gibbs free energy $G(P,T,N)$ is defined by $\mathcal{A} + PV$. Thus,

$$G(P,T,N) = - k_B T \ln Q + Pv \qquad\qquad (7.2.22)$$

Planck function Ψ is given by $\mathcal{A}(V,T,N) /T = \Psi$. All the thermodynamics is embodied in Ψ. Boltzmann constant permits relating to the quantum structure of the system via the energy spectra found in the partition function.

The question for us is to work a connection between the characteristic frequencies and the underlying quantum structure.

The functionality of the occupation (population) numbers n_k must be investigated. If eq.(7.1.5) define them, it is apparent that they will depend upon volume, temperature and total number of particles.

The import of partition functions is due to the fact that all equilibrium statistical properties of a system can be obtained from their derivatives. To simplify notations let us call $\beta = \beta(T) = 1/ k_B T$.

The average energy as a function of q is given as:

$$\partial \ln q/\partial \beta = (1/q)(\partial q/\partial \beta) = (1/q) \, \partial(\Sigma_k \exp(-\beta \varepsilon_k)/\partial \beta =$$

$$- \; (\Sigma_k \varepsilon_k \; \exp(-\beta \varepsilon_k) \, (1/q)$$

Multiply by N both members:

$$N \, \partial \ln q/\partial \beta = - \, \Sigma_k \varepsilon_k \exp(-\beta \varepsilon_k) N(1/q) =$$

$$-\Sigma_k n_k \varepsilon_k = -U \qquad\qquad (7.2.23)$$

Note that we use now the symbol for internal energy U to replace our initial average energy <E>. This is justified by the equality $N \, \partial \ln q/\partial \beta = -U$ in the sense that the distribution $\exp(-\beta \varepsilon_k)N(1/q)$ actually would maximize entropy submitted to constraints; this has to be shown (see below). We see that the partition function for the N-system will be $q^N = Q$. This agrees with a sum-over-states and not over particles as commented above. Thus,

$$U = - \, \partial \ln Q/\partial \beta \qquad\qquad (7.2.24)$$

In terms of the numbers $p_i = n_i/N$, that using standard language are taken as a propensity to populate the i-th state, we get:

$$<e> = - \partial \ln q / \partial \beta \qquad (7.2.25)$$

The average energy per particle in thermal equilibrium is just the derivative of the natural logarithm of the molecular partition function with respect to $\beta(T)$. It is a property depending upon the energy spectrum of the Hamiltonian operator H taken in a restrictive sense; it is usually assumed to be a molecular Hamiltonian; this issue will be discussed later on.

In thermodynamics, for an isolated system where the total energy E is conserved, the thermodynamic variables can be volume, entropy and particle number, that is U=U(V,S,N). So far we can obtain an energy $N<e(V,T)> = <E> \rightarrow$ E(V,T,N). Entropy S must be incorporated in the statistical mechanical level. Therefore, it is important to define the thermodynamic conditions valid for the statistical mechanics model. This can be done with the help of some thermodynamic potentials. The objective is the construction of two entropy state functions, S(V,E,N) and S(V,<E>,N), and find out conditions to equated them.

7.3. Thermodynamic potentials

In thermodynamics we start from an energy conservation postulate; one focus on variations of energy. Two mechanism are used to alter the internal state of the system: work δW done by or onto the system and exchange of heat, δq , thus

$$\delta U = \delta W + \delta q.$$

Both terms in the sum depend upon the way (path) taken to change the thermodynamic state of the system.

Select the class of reversible processes and mechanical model: $\delta W = -P \, dV$. Absolute temperature permits defining entropy, S, used as integrating factor:

$$\delta q / T = dS.$$

For reversible processes where the pressure P and temperature T are defined and fixed, the internal energy U is a function of volume and entropy: U(V,S). We add the dependence on particle number through the term μdN; μ is the chemical potential, i.e. the change in energy when particle number changes by one unit. Thus, one should write: U(V,S,N); and because it is a state function we write the differential form as:

$$dU(V,S,N) = (\partial U/\partial V)_{S,N} \, dv + (\partial U/\partial S)_{v,N} \, dS + $$

$$(\partial U/\partial N)_{v,S} \, dN \qquad\qquad (7.3.1)$$

From the first law examined above one can write an explicit equation:

$$dU = -P \, dv + T \, dS + \mu \, dN \qquad\qquad (7.3.2)$$

Comparison of these two equations shows that:

$$(\partial U/\partial v)_{S,N} = -P,$$

$$(\partial U/\partial S)_{v,N} = T \text{ and}$$

$$(\partial U/\partial N)_{v,S} = \mu \qquad\qquad (7.3.3)$$

These are named as thermodynamic potentials.

It is worth note that the variation of internal energy U with entropy equals absolute temperature; on the other hand, 1/T corresponds to $(\partial S/\partial U)_{v,N}$; it is the way entropy changes with internal energy that defines the inverse of the absolute temperature. In the Boltzmann factor (1/T) we have indirectly connected entropy to variations with internal energy. The internal energy can be made a function of entropy: $\langle E \rangle \rightarrow U(v,S,N)$ if energy $\langle E \rangle$ is constant.

Whenever we have special cases where processes at constant energy E are equivalent to processes at constant temperature with $\langle E \rangle$ having a fix limit E; then we can introduce comparisons between these two different ways to describe thermodynamic systems. Another way to say it is that the microcanonical and canonical ensembles are equivalent under specified conditions (see below).

Helmholtz free energy compared to the internal energy corresponds to a set of variables where entropy is replaced by absolute temperature. To achieve the change of variables proceeds as follows:

$$\mathcal{A}(v,T,N) = U(v,S,N) - TS \qquad\qquad (7.3.4)$$

In terms of differentials one gets:

$$d\mathcal{A}(v,T,N) = dU(v,S,N) - TdS - SdT = $$

$$-P \, dv + TdS - TdS + SdT + (\partial U/\partial N)_{v,S} \, dN \qquad (7.3.5)$$

Finally:

$$d\mathcal{A}(v,T,N) = -Pdv - SdT + (\partial A/\partial N)_{v,T}\, dN =$$

$$-Pdv - SdT + \mu\, dN \qquad\qquad (7.3.6)$$

Observe that $(\partial A/\partial N)_{v,T}$ is the chemical potential (numerical value).

For Gibbs free energy G when compared to Helmholtz free energy, the volume V is changed into pressure P:

$$G(P,T,N) = \mathcal{A}(v,T,N) + Pv \qquad\qquad (7.3.7)$$

This closes the presentation of thermodynamic aspects. It is interesting to realize that the ensemble concept actually permits the establishment of relation ships with thermal types of quantum states. Although the phases are not accessible, the relative intensities are obtained from statistical analyses.

Irreversible processes can also be incorporated as shown by Jaynes. As we suggest with eq. (7.1.11) the time evolution of quantum states included in a non-reversible ensemble would permit handling phenomena at the Fence.

7.4. Thermal equilibrium and radiation

Electromagnetic radiation is inseparable from electrically charged matter. The interaction between them corresponds to changes of their quantum states. Energy is emitted or absorbed by material systems at a given temperature in the form of radiation of the electromagnetic type, e.g. visible, infrared, microwave are just radiation types characterized by frequency ranges. The product of frequency (ν) and wavelength (λ) in vacuum is equal to the speed of light c.

$$\lambda\nu = c \qquad\qquad (7.4.1)$$

The eq.(7.4.1) hides the quantum nature of light. For, $h\nu$ is a quantum of energy related to the frequency, h is Planck constant, and λ/h is the inverse of linear momentum, $1/k$, of the electromagnetic wave. Then, (7.4.1) can be read as follows:

$$E_\nu = hc\,(1/\lambda) = k\,c \qquad\qquad (7.4.2)$$

The wave number ($1/\lambda$) is of course ν/c and the momentum of the electromagnetic wave is just de Broglie relationship $k = h/\lambda$. The energy is quantized; the number of photons for a given frequency is the equivalent to the occupation numbers we have been using.

Consider a collection of N energy levels that are sustained by a material system that at temperature T have amplitudes squared proportional to Boltzmann

factors. If the degeneracy of the level is m_i the Boltzmann distribution function one can write:

$$f_i(E_i) = C_d(T) \, m_i \exp(\beta \, E_i)$$

where

$$C_d(T) = 1/(\Sigma_i \, m_i \exp(\beta \, E_i)) = 1/q.$$

The occupation number being $N_i = f_i(E_i) \, N$ and, of course, $\Sigma_i \, N_i = N$. In order to induce a form valid for more general cases, the occupation number for the discrete level case is written as:

$$N_i = N \, C_d(T) \, m_i \exp(\beta \, E_i) \qquad\qquad (7.4.3)$$

For high-density materials energy levels are almost continuously distributed (for all practical purposes) we transform N_i into the number of energy levels $g(E)$ in the energy shell E, $E+dE$: $g(E)dE$ and equate it to $C_c \exp(-\beta E) \, dE$; the sub index c refers to a continuum case. In the standard interpretation, this equation corresponds to a relative frequency, probability, of finding a fraction of the given material excited at a specific energy E in the energy shell dE. Adding the contributions from $E=0$ up till very high energy $E=\infty$, we get the normalization condition:

$$\int_0^\infty g(E)dE = \int_0^\infty C_c \exp(-\beta E) \, dE =$$
$$\int_0^\infty (C_c/\beta) \exp(-\beta E) \, d\beta E) = 1 \qquad\qquad (7.4.4)$$

Thus, with $(C_c/\beta)=1$ one obtains:

$$g(E) = \beta \exp(-\beta E) = (1/k_B T) \exp(-\beta E) \qquad (7.4.5)$$

The occupation number (or number of atoms if you like) at energy E within an energy shell is given by

$$N(E) \, dE = N/k_B T \exp(-E/k_B T) \, dE \qquad\qquad (7.4.6)$$

The ratio in occupation numbers (populations) between two energy shells $N(E_1)$ and $N(E_2)$ is just

$$N(E_2)dE/N(E_1)dE = N(E_2)/N(E_1) =$$
$$\exp(-\Delta E_{21}/k_B T). \qquad\qquad (7.4.7)$$

For high-density matter where, for all practical purposes, occupation numbers vary in a continuous fashion thermal equilibrium is achieved everywhere.

We can count the occupation number, for instance, above a given energy threshold E_{thr} as follows:

$$N(\text{above threshold}) =$$
$$(N/k_B T) \int_{E=Ethr} \exp(-E/k_B T) \, dE \qquad\qquad (7.4.8)$$

The upper limit is $E=\infty$.

E&E.7-1 Determine the temperature required for the quantum state to show occupation numbers different from zero in the energy region corresponding to visible light. Assume, for a typical material $N = 5 \times 10^{28}$ atoms/m^3

We have then a simple correspondence between fully discrete and quasi-continuum spectra. We handle some specific aspects of radiation and thermal equilibrium. We want to have a description of blackbody (BB) radiation. For this reason, some macroscopic variables must be introduced.

Stefan-Boltzmann law: The intensity I or the total radiation intensity (W/m^2) emitted from a body at temperature T is proportional to the fourth power of the temperature, T^4: $I = e_M \sigma T^4$. The emissivity e_M is a property of given material; σ is a constant equal to 5.67x10-8 W/m^2-K^4. Remember that W in Watts is energy per time, power. Planck constant is energy by time, action. The emissivity has no dimension; it represents the ability of a body to radiate efficiently and also is associated with its ability to absorb radiation.

There are two concepts of interest: *radiance* (H) and *irradiance* (I). The irradiance, I, is the energy emitted by a body; thus, a change of the occupation numbers of the body is detected, in the decreasing direction (those excited levels lose energy). The radiance impinging on a body, irradiance, changes the occupation numbers; not only there will be an increase in some of them, one may expect some excited levels to make an induced emission so that some level occupancy may go down. The radiance is proportional to the irradiance: $H = e_M I$ or $I = H / e_M$.

The perfect absorber also describes the perfect emitter, $e_M=1$. A perfect absorber is known as a blackbody. This, in turn, is the best emitter of thermal radiation; this radiation is known as blackbody radiation.

Blackbodies radiate with the same spectral power for that occurring within a *cavity*. One example of cavity may be a cubic box as the one used above.

The base states of a radiation field (Cf. Chapter 5) are those corresponding to harmonic oscillators of given frequency: $E_n(\nu) = h\nu(n+1/2)$. The quantum number n is the occupation number of the ground state: $|n,\nu\rangle$ corresponds to the base state of n-photons each with energy $h\nu$. A base state in a box is represented by a product involving the internal state (number of photons n) and the external (propagation in the box space) plane wave form.

$$|\mathbf{k}, n\rangle = \exp(k_1 L_1 + k_2 L_2 + k_3 L_3) |n, \nu\rangle \qquad (7.4.9)$$

The reciprocal vector $\mathbf{k}=(k_1,k_2,k_3)$ indicates the propagation direction of the electromagnetic wave and momentum; the box defines a fixed laboratory frame.

The problem is counting the number of cavity modes. A problem similar to the one discussed for particle-states in a box. Periodicity is ensured whenever

$$k_1 L_1 = n_1 \pi; \ k_2 L_2 = n_2 \pi; \ k_3 L_3 = n_3 \pi; \ n_1, n_2, n_3 = 0,1,2\ldots$$

Any mode in the cavity corresponds to a specific $\mathbf{k}$; the number of modes is obtained by specifying the integer numbers n_1, n_2, n_3 because:

$$\mathbf{k}^2 = k_1{}^2 + k_2{}^2 + k_3{}^2 =$$

$$\{ (n_1\pi/L_1)^2 + (n_2\pi/L_2)^2 + (n_3\pi/L_3)^2 \} \qquad (7.4.10)$$

The total number of modes in a volume $v = L_1 L_2 L_3$ for a given wavelength $\lambda = 2\pi/k$ can hence be counted in a manner similar to particle-state in a box. The volume of the octant is:

$$(1/8)\,(4\pi/3)\,(n_1\,n_2\,n_3) =$$

$$(1/8)\,(4\pi/3)\,(2\,L_1/\lambda)(2L_2/\lambda)(2L_3/\lambda) = v/8\,(4\pi/3)(2/\lambda)^3.$$

The number of modes W_ν can be cast in terms frequency:

$$W_\nu = v/8\,(4\pi/3)(2/\lambda)^3 = (4/3)\,\pi\nu^3/c^3\,v \qquad (7.4.11)$$

This number represents the number of modes for all frequencies up to the frequency ν within the volume v. This number must be doubled to take into account polarization; light has spin 1 but only two components express due to the zero rest mass. The density $\rho(\nu)$ or number of modes per unit volume is then given by:

$$\rho(\nu) = 2\,W_\nu/v = (8/3)\,\pi\nu^3/c^3 \qquad (7.4.12)$$

Calculate now $\rho(\nu+\delta\nu) - \rho(\nu)$, that is the number of frequencies in the frequency shell:

$$d\rho(\nu)/d\nu = 8\,\pi\nu^2/c^3 \qquad (7.4.13)$$

The energy per mode $u(\nu)$ is given by $d\rho(\nu)/d\nu$ multiplied by the average energy at temperature T:

$$u(\nu) = d\rho(\nu)/d\nu\, \langle n_\nu \rangle = 8\,\pi\nu^2/c^3\,(U_\nu - h\nu/2) =$$

$$(8\pi\nu^2/c^3)\,(h\nu\,/(\,\exp(h\nu/k_BT)-1) \qquad (7.4.14)$$

$u(\nu)$ describes the energy density per unit frequency ν for radiation anywhere within an enclosed cavity at a temperature T. In the cavity, travelling waves are found in all directions. The total energy density u emitted at all frequencies is given by:

$$u = \int_0^\infty u(\nu)\,d\nu \qquad (7.4.15)$$

The result of integration is Stefan-Boltzmann.

Let us relate the energy density to the intensity $I(\nu)$:

$$I(\nu) = c\,u(\nu) \qquad (7.4.16)$$

The blackbody emission, total radiance $I_{BB}(\nu)$ from the frequency interval $d\nu$ is given as:

$$I_{BB}(\nu) \, d\nu = (c \, u(\nu)/4) \, d\nu =$$

$$2\pi h \nu^3/c^2 \, d\nu \, /(\exp(h\nu/k_BT) - 1) \qquad (7.4.17)$$

Finally, $|d\nu| = (c/\lambda^2) \, d\lambda$ and one can define an $I_{BB}(\lambda,T)$.

E&E.7-2. Calculate explicitly $I_{BB}(\lambda,T)$.

(Answ. $I_{BB}(\lambda,T) = 2\pi hc^2 \, \lambda^{-5} \, (\exp(ch/\lambda k_BT) - 1)^{-1}$.

The total radiance emitted from the blackbody surface within a wavelength interval $\Delta\lambda$ is given by:

$$I_{BB}(\lambda,\Delta\lambda,T) = I_{BB}(\lambda,T) \, \Delta\lambda \qquad (7.4.18)$$

E&E.7-3. Show that for $\Delta\lambda$ in nano meters, λ in meters and T in degrees Kelvin, then

$$I_{BB}(\lambda,T) = (3.75 \times 10^{-25}) \, \lambda^{-5} \, (\exp(0.0144/\lambda T) - 1)^{-1} \, W/m^2\text{-nm}$$

E&E.7-4. Calculate the radiation power $P = I_{BB}(\lambda,T) \, \Delta\lambda \, \Delta A$ coming from a surface (ΔA) at temperature 300K and area 0.02 m^2 over a wavelength interval of 0.1μm at a wavelength of 1.0 μm.

Hint: Change $I_{BB}(\lambda,T)$ above to W/m^2-μm

Answ. 1.06×10^{-15} W.

E&E.7-5. Change the temperature up to T=1000K and calculate the radiation flux or power as in the preceding exercise.

7.5. Spontaneous emission at radio frequencies

For nuclear magnetic resonance (NMR) transition amplitudes T_ν at radio frequencies for spontaneous emission lead to a corresponding probability A_ν given by:

$$A_\nu = (8\pi\nu^2/c^3) \, h\nu \, (8\pi^3\mu^2/3h^2) \, \sec^{-1} \qquad (7.5.1)$$

As pointed out by Purcell this is so small a quantity that the process is not effective in bringing a spin system into thermal equilibrium with its surroundings. But he also noted that for a system coupled to a resonant electrical circuit, the factor ($8\pi\nu^2/c^3$) no longer gives correctly the number of radiation oscillators per unit volume, in unit frequency range; now there is one oscillator in the frequency range associated to the circuit. The spontaneous probability is hence increased so that the mechanism should be able to establish thermal equilibrium in a time of the order of minutes and not 10^{21} minutes as was in the preceding case.

It is this type of effect that will be used to modulate life times of quantum states below.

7.6. Model Systems: Partition functions

Consider the harmonic oscillator at frequency ν. The enermy is hν, where h is Planck constant.

$$\varepsilon_k = (k+1/2) h\nu \quad \text{and} \quad k=0,1,2,\ldots$$
$$q = \Sigma_k \exp(-(k+1/2) h\nu\beta) =$$
$$\exp(-(1/2) h\nu\beta) \Sigma_k \exp(-k \, h\nu\beta) \qquad (7.6.1)$$

Put h$\nu\beta$ =x = hν/k_BT to get:

$$q = \exp(-(1/2) x)\Sigma_k \exp(-k \, x) =$$
$$\exp(-(1/2) x)1/(1-\exp(-x)) =1/2\sinh(x/2) \qquad (7.6.1')$$

Note that $\exp(-k \, x)= (\exp(-x))^k$ and the result follows from standard algebra, i.e. geometric progression. The partition function reads:

$$q= \exp(-(1/2) h\nu/k_BT) (1/(1-\exp-h\nu/k_BT)) \qquad (7.6.1'')$$

The Helmholtz free energy $\mathcal{A}$ per particle is

$$= k_BT (1/2) x - k_BT \ln(1-\exp(-x))^{-1} =$$
$$h\nu/2 + k_BT \ln(1-\exp(-h\nu/k_BT)) \qquad (7.6.2)$$

It is of interest to label the frequency also. There are many physical systems where the frequency is quantized. For normal modes this would be a natural choice. If we change the unit of frequency from an inverse of time to circular frequency for the i-th mode, $2\pi\omega_i = \nu_i$, Planck constant is then "rationalized" by taking it to be h/2$\pi = \hbar$, then hν_i =$\hbar\omega_i$. Circular frequency is more often used in spectroscopy.

$$\mathcal{A}_i = -k_BT \ln q_i =$$

$$\hbar\omega_i /2 + k_BT \ln(1-\exp(-\hbar\omega_i /k_BT)) \qquad (7.6.3)$$

The total free energy is then

$$\mathcal{A} = \Sigma_i \ \mathcal{A}_i =$$

$$\Sigma_i \ \{\hbar\omega_i /2 + k_BT \ln(1-\exp(-\hbar\omega_i /k_BT))\} \qquad (7.6.4)$$

The average energy of a single oscillator U_i in thermal equilibrium is given by:

$$U_i = (1/q_i) \ \Sigma_k \ \varepsilon_k^i \exp(-\varepsilon_k^i \ \beta) = \partial \ (\mathcal{A}_i \ /\beta)/\partial\beta =$$

$$\hbar\omega_i /2 + \hbar\omega_i /(\exp(\hbar\omega_i /k_BT) -1) \qquad (7.6.5)$$

The total energy U is given by the sum:

$$U = \Sigma_i \ U_i =$$

$$\Sigma_i \ \{\hbar\omega_i /2 + \hbar\omega_i /(\exp(\hbar\omega_i /k_BT) -1) \ \} \qquad (7.6.6)$$

Taking away the zero-point energy, U-ZPE can be written as $\Sigma_i \ \hbar\omega_i /(\exp(\hbar\omega_i /k_BT) -1)$. If we define the average occupation number of the i-th mode as $<n_i>$:

$$<n_i> = 1 /(\exp(\hbar\omega_i /k_BT) -1). \qquad (7.6.7)$$

This is the average occupation number at temperature T. Planck proposed it on experimental grounds by 1900. Now, eq.(A30') reads:

$$U = \Sigma_i \ \hbar\omega_i \ (1/2 +<n_i>) \qquad (7.6.8)$$

The statistical distribution looks like an infinite set of oscillators with non-integer occupation numbers $<n_i>$ for this normal (field) mode. As a matter of fact such is not the case because we are overlooking the fact conveyed by the averaging operation. This means that we have prepared the quantum state of the EM field with a definite amount of energy. The wave function would take care of such situation. The ZPE is operating in Fock (Hilbert) space and serves the purpose to convey the set of frequencies that are actually been activated. This trick underlies the difficulties associated with mixing the levels of description. As we already know one cannot eliminate the vacuum base state at a given frequency by at the level of counting energy exchanged the ZPE cancels out.

The above calculations permit appreciating the type of analyses required in quantum statistics. We give now an overview of classical statistics.

7.7. Classical Statistical Mechanics

The construction of a partition function is the key element to construct statistical distribution. The quantum case appears fairly simple yet the actual calculation of energy levels may be a daunting task. The place of a partition function is taken by the time dependent density   defined over the atomic and momentum coordinates as arguments: $\mathbf{r}=(\mathbf{r}_1,\ldots,\mathbf{r}_N)$ and $\mathbf{p}=(\mathbf{p}_1,\ldots,\mathbf{p}_N)$. So far focus has been on quantum

aspects but now we move to a Fence like system where classical mechanics drives the dynamics on the N-particles inside a volume v. A brief review of classical mechanics follows.

7.7.1. Elements of Classical Mechanics

The inertial frame associated to a given quantum system belongs to real space. One way or another, the classical formalism must be considered. We have signaled the material system as sustaining the quantum states but now seem appropriate to have a look to this material aspect in real space.

Let us paraphrase Newton's axioms putting the emphasis in our language:

First axiom: *a material system remains at rest, or in uniform motion, if no external forces act to change its state of motion.*

Second axiom: *the change in the state of motion of a material system is proportional to the force that acts on the body, and takes place in the direction of the force.*

This is the famous Newton's second law. We note that the state of motion represented by the momentum **p** of the material system is conserved in absence of external interactions.

The third axiom concerns the law of action and reaction. There are two more axioms that concern absolute time and absolute space, respectively. They read as follows: *time flows equally, without relation to anything external and there is an absolute time*; *absolute space, without relation to anything external, remains always similar and immovable*.

Once a reference frame is introduced, **r** defines the position of the I-frame. The second quantity defining the fundamental state of motion is its momentum **p**. Thus, the rate at which **p** changes in time, namely, d**p**/dt signals the presence of an external force **F**. The second axiom takes on the mathematical form:

$$\mathrm{d}\mathbf{p}/\mathrm{d}t - \mathbf{F} = \mathbf{0} \qquad\qquad (7.7.1.1)$$

The pair (**r**,**p**) is a point in the phase space; a volume element in this space, d**r**d**p** has dimension of Action.

In non-relativistic mechanics, the velocity of the I-frame, **v**=d**r**/dt, when the total mass M is located at the origin, the linear momentum is proportional to the velocity; M plays the role of proportionality constant; **p** = M**v**. Newton second law reads now:

$$\dot{r} = \mathbf{v} \ , \quad \dot{p} = \mathbf{F} \qquad\qquad (7.7.1.2)$$

In so far the action is concerned, the momentum and position coordinates are known as canonically conjugated. The classical Hamiltonian function $H(\mathbf{r},\mathbf{p},t)$ with dimension of energy is canonically conjugate with time. For an isolated system with mass M, the (kinetic) energy is given by $\mathbf{p}^2/2M$, in presence of scalar potential $U(\mathbf{r},t)$ and a vector potential $\mathbf{A}(\mathbf{r},t)$ the Hamiltonian is given by:

$$H(\mathbf{r},\mathbf{p},t) = (1/2M)\,(\mathbf{p} - \mathbf{A}(\mathbf{r},t))^2 + U(\mathbf{r},t) \qquad (7.7.1.3)$$

If there is no vector potential modulating the I-frame particle momentum, Hamilton equation of motion follow directly from eq.(7.7.1.2) and (7.7.1.3):

$$\dot{r} = \mathbf{\nabla}_{\mathbf{p}}\, H(\mathbf{r},\mathbf{p},t) \quad \text{and}$$

$$\dot{p} = -\mathbf{\nabla}_{\mathbf{r}}\, H(\mathbf{r},\mathbf{p},t)\,. \qquad (7.7.1.4)$$

The pair of potentials $(\mathbf{A},U)$ in eq.(7.7.1.3) are called a gauge. Two gauges leading to the same motion in configuration space are equivalent.

The equations (7.7.1.4) permit the study of transformations in phase space from a given point $(\mathbf{r}',\mathbf{p}')$ at time t' into $(\mathbf{r},\mathbf{p})$ at time t; the intermediate values in phase space form a trajectory Γ. This trajectory relates two points in phase space in the time lapse (t-t') so that we do not have a problem with absolute time or space; this is an important point. The action $A(\Gamma)$ along the trajectory is defined by the integral along the trajectory by:

$$A(\Gamma) = \int_{\Gamma} (\mathbf{p}\cdot d\mathbf{r} - Hdt) \qquad (7.7.1.5)$$

The question is whether or not an action function can be defined with trajectories in configuration space only. You remember that in the preceding sections the quantum states were projected in configuration space. Here we follow de Gosson analysis: if time t-t' is sufficiently small, then the phase space arc G projects diffeomorphically onto a curve γ without self-intersections in configuration space $\mathbf{R}_{\mathbf{r}}^3$ that connects $\mathbf{r}'$ at t' with $\mathbf{r}$ at t. The projection is bi-univoque so that γ (real space) uniquely determines Γ (phase space). The integral (7.7.1.5) can safely be performed with paths belonging to $\mathbf{R}_{\mathbf{r}}^3 \times \mathbf{R}_t$.

Besides entering some important definitions of classical analytical dynamics, the mapping between phase space and configuration space is fundamental. A second aspect concerns Liouville Theorem. The connection between $\mathbf{r}'$ at t' with $\mathbf{r}$ at t defines a mapping f_t that is volume preserving. A ball B in phase space with radius R and origin $(\mathbf{r}_o,\mathbf{p}_o)$ can be analyzed by looking at projections over different planes; the result is a disk that, for instance in the (y,p_y) and (y,p_z) planes one gets, respectively:

$$(y-y_o)^2 + (p_y-p_{yo})^2 \leq \pi R^2 \quad \text{and}$$

$$(y-y_o)^2 + (p_z-p_{zo})^2 \leq \pi R^2.$$

Gromov, as cited by de Gosson, made the extraordinary discovery that the canonically conjugated shadows never become smaller that their respective πR^2, while the non-conjugated shadows can be made arbitrarily small. This is a non-squeezing property that was not known before 1985! These results are a sort of equivalent of Heisenberg's inequalities that imply that Hamiltonians flows on phase space volumes are much more "rigid" than that of straight volume preserving diffeomorphisms.

We come back to our I-frame systems. Let the material systems associated to each I-frame have masses M_1, M_2,... and quantum states derived from Hamiltonian operators $\hat{H}_1$, $\hat{H}_2$,... with no interactions among those subsystems. Each subspace shows complete sets of base states, in particular those derived from the self-adjoint Hamiltonian operators. At the Fence, there are three possibilities in so far fenomenological descriptions are concerned. Case one: consider the I-frame systems as classic each one having the total mass located at the origin the whole without interactions. Case two: include interactions while keeping the I-frame classic. Case three: attempt real space quantization procedures, e.g. box quantization.

Before entering a quantum mechanical analysis let us introduce classical mechanical aspects first. This will not only help introducing classical dynamics language but constitute a widely used simulation technique.

At the Fence the I-frames carry (support) quantum states that in view of the inertial nature of the frame cannot distinguish the state of motion. Seen from a fixed laboratory frame, each I-frame displays a velocity $\mathbf{v}_i$. There is more. Construct the product between $M_i c$ and ds_i; $ds_i = +cdt \sqrt{1-v_i^2/c^2}$ that are well defined provided the internal quantum states do not change. To get the differential of the action dA_i we equate this to $M_i ds_i$. Integrating over the trajectories initiating at point $\mathbf{R}_i$' at time t' and ending at $\mathbf{R}_i$'' at time t'' on the action functional $A[\gamma]$ is defined as:

$$A[\gamma] = -\int_{\mathbf{R}i',t'}^{\mathbf{R}i,t} M_i c\, ds_i =$$
$$-\int_{t'}^{t''} M_i c\, (ds_i /dt)\, dt =$$
$$-\int_{t'}^{t''} dt\, M_i c^2 \sqrt{(1-v_i^2/c^2)} \qquad (7.7.1.6)$$

In classical mechanics the integrand of (7.7.1.1) corresponds to the Lagrangian function L:

$$L(\mathbf{R}_i, \dot{R}_i, t) = - M_i c^2 \sqrt{(1-v_i^2/c^2)} =$$
$$- M_i c^2 + (1/2) M_i \mathbf{v}_i^2 + O(v_i^4/c^2) \qquad (7.7.1.7)$$

In what follows we use $\dot{R}_i = \mathbf{v}_i$. The linear momentum of the i-th inertial frame is defined by:

$$\mathbf{P}_i = \partial\, L(\mathbf{R}_i, \mathbf{v}_i, t)/\partial \mathbf{v}_i \qquad (7.7.1.8)$$

Neglected the constant term $-M_i c^2$ because it is the variation δL that enters the analysis. Using (7.7.1.7) with (7.7.1.8) we can see that the classical state of motion will be $P_i = M_i v_i$. For such a sample, the total classical kinetic energy:

$$K = \Sigma_i (1/2) M_i v_i^2 = \Sigma_i (1/2M_i) P_i^2 \qquad (7.7.1.9)$$

The sum is over N, the number of I-frames; these are classical entities, recorded from the laboratory system their position vectors can be assigned: $R = (R_1,\ldots,R_i,\ldots R_N)$. To each of these points a momentum vector is assigned: $P = (P_1,\ldots,P_i,\ldots P_N)$. Also, the velocity v is defined by the vector $v = (v_1,\ldots,v_i,\ldots v_N)$.

The profound difference between vectors such as $R = (R_1,\ldots,R_i,\ldots R_N)$ where the tip of each R_i stands for the position with respect to the chosen I-frame of a particle endowed with mass M_i and the abstract configuration space we use to project quantum states. For now the tips of the configuration space stands as labels and nothing more. The labels enter the base vectors |labels> of a particular type of Hilbert space.

A fundamental concept of classical physics is the potential energy function allowing for interactions between I-frame systems and/or with external sources. This function is written in terms of the coordinate configuration: $V = V(R_1,\ldots,R_i,\ldots R_N)$ or in compact form $V(R)$.

The Lagrangian $L(v,R)$ for low speed (non-relativistic limit) and non-interacting system is just $K(v)$. Including interaction it reads:

$$L(v,R) = K(v) - V(R) \qquad (7.7.1.10)$$

We have now all the elements to construct an equation of motion for the system driven by the Lagrangian (7.7.1.10). First, the action over trajectories, A[trajectories], is a functional over trajectories relating the initial space-time point to the final one. There is one of those that render the action functional stationary. Let us calculate δA from the simple definition where the Lagrangian is time independent and functionally depend upon the trajectory $[l_i]$:

$$A[\lambda_i] = \int_{t_o}^{t_1} dt\, L(R_i, \dot{R}_i) \qquad (7.7.1.11)$$

The variation obtains as follows:

$$\delta A = \int_{t_o}^{t_1} dt\, L(R_i + \delta R_i, \dot{R}_i + \delta \dot{R}_i) - \int_{t_o}^{t_1} dt\, L(R_i, \dot{R}_i) \quad (7.7.1.12)$$

You can check that the constant $-M_i c^2$ cancels out. After expanding with Taylor theorem and some partial integration one gets:

$$\delta A = \int_{t_o}^{t_1} dt\, \delta R_i \{d(\partial L(R_i, \dot{R}_i)/\partial \dot{R}_i)/dt - \partial L(R_i, \dot{R}_i)/\partial R_i\}$$

$$(7.7.1.13)$$

The term in curly brackets must be zero because $\delta\mathbf{R}_i$ is arbitrary thereby leading to Euler-Lagrange equations:

$$d(\partial L(\mathbf{R}_i, \dot{R}_i)/\partial \dot{R}_i)/dt - \partial L(\mathbf{R}_i, \dot{R}_i)/\partial \mathbf{R}_i = 0 \qquad (7.7.1.14)$$

If we replace the Lagrangian eq. (7.7.1.5) one obtains Newton's equations:

$$d\mathbf{P}_i/dt = \dot{P}_i = - \partial V(\mathbf{R}_i)/\partial \mathbf{R}_i \qquad (7.7.1.15)$$

In phase space, $(\mathbf{P},\mathbf{R})$, the energy function is the Hamiltonian $H(\mathbf{P},\mathbf{R})$ defined by:

$$H(\mathbf{P},\mathbf{R}) = K(\mathbf{P}) + V(\mathbf{R}) \qquad (7.7.1.16)$$

The energy functions defined over spaces $(\mathbf{v},\mathbf{R})$ and $(\mathbf{P},\mathbf{R})$ are related via a Legendre transformation:

$$H(\mathbf{P},\mathbf{R}) = \mathbf{v} \cdot \mathbf{P} - L(\mathbf{v}(\mathbf{P}),\mathbf{R}) \qquad (7.7.1.17)$$

And

$$L(\mathbf{v}, \mathbf{R}) = \mathbf{v} \cdot \mathbf{P} - H(\mathbf{P},\mathbf{R}) \qquad (7.7.1.18)$$

In phase space, the equations of motion, named as Hamilton equations read:

$$\dot{P}_i = \partial H/\partial \mathbf{R}_i \text{ and } \dot{R}_i = \partial H/\partial \mathbf{P}_i \qquad (7.7.1.19)$$

The second equation is the definition of velocity in phase space. The first formula embodies Newton second law. In classical mechanics, its momentum characterizes the physical state. The change in time ($\dot{P}_i$) elicits the action of an external force ($\partial H/\partial \mathbf{R}_i$).

7.7.2. Statistical ensembles

At the Fence, the classical dynamics of I-frames, for which their internal quantum states permit representing the total mass of the material system as if it were at the frame origin, can be simulated with molecular dynamics techniques. The interaction potential depends upon the (internal) quantum states; which is a natural result of the present approach. For the time being assume that $V(\mathbf{R})$ has no mechanism to induce changes of quantum states in the I-frame systems

The N non-interacting I-frame-systems occupy a given volume v. The control of these parameters is made in the laboratory; this includes the type of I-frame systems included in given experiments. The thermodynamic limit can be defined: limit (N/v) equals to a constant when both N and v increases without boundaries. The density function is hence time independent: $\rho(\mathbf{r},\mathbf{p})$. This equilibrium density permits determination of average values of functions over phase space:

$$<F> = \int \ldots \int (d^3\mathbf{r} \, d^3\mathbf{p} \, /\hbar^{3N}) \, F(\mathbf{r},\mathbf{p}) \, \rho(\mathbf{r},\mathbf{p})$$

W is a constant determined by normalization of the density function an is equal to V/N because we take:

$$\int\ldots\int(d^3\mathbf{r}\, d^3\mathbf{p}\, /\hbar^{3N})\, \rho(\mathbf{r,p}) = 1$$

For the canonical ensemble one has the partition function:

$$Q = \int\ldots\int(d^3\mathbf{r}\, d^3\mathbf{p}\, /\hbar^{3N})\, \exp(-H(\mathbf{p,r})\, \beta)$$

$\beta=1/k_B T$ The average value <F> is given by:

$$<F>(T) = \int\ldots\int(d^3\mathbf{r}\, d^3\mathbf{p}\, /\hbar^{3N})$$
$$[\exp(-H(\mathbf{p,r})/k_B T)/Q]\, F(\mathbf{r,p})\, /\, Q$$

By analogy with the quantum physical case, all thermodynamic functions can be obtained from the partition function. Note $Q^{-1}\, \partial Q/\partial \beta = <\, H(\mathbf{p,r})>$. Formally, one can recover all thermodynamic potentials from the partition function. This closes our overview on this subject.

Fence space may remain as real 3-space with quantized internal states. The concept of distance and shape can geometrically be implemented. Arrays simulating crystals, quasi-crystals, surfaces can be constructed following symmetry patterns; perfect gases correspond to V(**R**)=0, no inter-I-frames interactions. Surfaces with quantum dots can be represented by substituting at given places with an I-frame system that stands for a default (quantum dot). Molecular beam experiments can be described using mixed schemes. These latter are especial cases to be found in scattering theory. These examples are given to illustrate a class of systems one can, in laboratory conditions, represent where quantum aspects can be partially incorporated.

7.7. Concluding remarks

This short chapter illustrates the subsidiary character of classical statistical mechanics where phase space plays a central role. All statistical formulae derive from energy levels, occupation numbers and Shannon theorem as implemented by Jaynes.

Gathering results from present day technology it is quantum physics that informs the basic mechanism allowing for construction of all kinds of new devices.

The point is the following: It is quantum physics that occupies center stage that is clearly detrimental to the apodicticity of classical physics. The latter might be simpler to solve a number of problems compared to a quantum approach. Yet, at the end of the day, the fundamental mechanisms are quantum physical in nature. A simple conclusion appears to be: the world (universe) where we work constructing scientific views is quantum physical in nature. The endeavors

expended in finding mechanism allowing for emergence of a classical world from a quantum one are probably missing the point.