Chapter 9

Statistical Mechanics and Path Integrals

So far we have been discussing some well defined quantum states and transitions between them. However, in real experiments we are usually dealing with mixtures of states. Very often we can reasonably assess probabilities of their occurences and through a process of averaging take care of such uncertainties.

In this Section we are going to deal with one of the most important statistical distributions of quantum states: a system in thermal equilibrium with a given temperature T. Since, according to Gibbs, the probability, p_i, of having our system in the state of energy E_i is

$$p_i = \frac{1}{\mathcal{Z}}\, e^{-\beta E_i} \tag{9.1}$$

where $\beta = (k_B T)^{-1}$, k_B being the Boltzmann constant, and the normalization factor (the so called partition function) $\mathcal{Z}$ equals

$$\mathcal{Z} = \sum_i e^{-\beta E_i}\,. \tag{9.2}$$

It is important to construct an (Euclidean) analogue of the Feynman propagator which is called the density matrix

$$\rho(x_2, x_1, \beta) = \sum_i \phi_i(x_2)\phi_i^*(x_1)\, e^{-\beta E_i}\,. \tag{9.3}$$

Here $\phi_i(x)$ is the eigenfunction corresponding to the energy E_i.

From our earlier discussions of Euclidean propagators we know how to write (9.3) as a functional integral:

$$\rho(x_2, x_1, \beta) = \int [\mathcal{D}_E x(\tau)]\, e^{-\frac{1}{\hbar}\int\limits_0^{\beta\hbar} \mathcal{H}(x(\tau))d\tau}\,. \tag{9.4}$$

Having ρ we can calculate all thermodynamic functions of the system and have also its complete quantal description. For instance

$$\mathcal{Z} \;=\; \int dx \rho(x, x, \beta) \;=\; \mathrm{Tr}\,\rho \;=\; e^{-\beta F} \tag{9.5}$$

where F is the free energy. Let us go quickly through definitions of some important thermodynamic functions a relations between them.

The average energy of a system is

$$U = \sum_i p_i E_i = -\frac{1}{\mathcal{Z}}\frac{\partial \mathcal{Z}}{\partial \beta} = F + \beta\frac{\partial F}{\partial \beta} = \frac{\partial}{\partial \beta}(\beta F) = F - T\frac{\partial F}{\partial T}\,. \tag{9.6}$$

Partial derivatives of the free energy, F, with respect to various parameters (like temperature, volume, external potentials of various kinds) give us "forces". For instance:

$$\text{entropy} \qquad S = -\left.\frac{\partial F}{\partial T}\right|_V \tag{9.7}$$

$$\text{pressure} \qquad P = -\left.\frac{\partial F}{\partial V}\right|_T\,. \tag{9.8}$$

Therefore (9.6) can also be written as

$$U = F + TS\,. \tag{9.9}$$

On the other hand, the expectation value of any observable A of the sytem in thermal equilibrium is

$$\langle A \rangle = \frac{\mathrm{Tr}\,[A\rho]}{\mathrm{Tr}\,\rho} \tag{9.10}$$

where we have used a notation which removes the dependence of our expressions on a representation used. Indeed,

$$\langle A \rangle = \int dx \sum_n \phi_n^*(x) A \phi_n(x)\, \frac{e^{-\beta E_n}}{\mathcal{Z}} \tag{9.11}$$

where

$$\begin{aligned}\int dx \sum_n \phi_n^*(x)\, A\, \phi_n(x)\, e^{-\beta E_n} &= Tr\left[\int dx' A_{x'',x'} \sum_n \phi_n(x')\phi_n^*(x)\, e^{-\beta E_n}\right] \\ &= \mathrm{Tr}\,[A\rho]\,.\end{aligned}$$

The relation between the Feynman propagators and the density matrices following from (9.3), (9.4)

$$\rho(x_2, x_1, \beta) = K(x_2, x_1, -i\hbar\beta)\,, \tag{9.12}$$

although nobody doubts its correctness, is not well understood. Comments of Feynman [10.1]: "*...the derivation of this result requires noting the wave equation, the existence of stationary states and eigevalues... all of which leads to the expression (9.12). Finally, we proceed to the reverse argument producing the path integral formulation for ρ. Is there any way to derive the path integral expression for $\mathcal{Z}$ (or ρ) for a system in equilibrium directly from the path integral description for the time-dependent motion? Can we find a short cut which* *avoids the mention of energy levels altogether? If it is possible, we do not yet know how to do it.*" Comments of Polyakov [10.2]: "*Our derivation of these analogies, (9.12) , was technical. I feel that there are deep reasons for them, connected with the properties of space-time. Although no real explanation exists, I shall give some comments on this below, when discussing gravity.*"

In any case (9.12) leads to a description of a thermal equilibrium with the help of the parameter $\hbar\beta = \hbar/k_B T = \mathcal{T}$ which has dimension of time. This may cause some discomfort since a system in thermal equilibrium leads a *time independent existence*. We may find an equivalent time independent description of *e.g.* nonrelativistic particles in equilibrium when we accept that in space-time a particle is identified with a string, $x(t) \to x(t,l)$ (for the sake of illustration we take one time and one space dimensions: t and l). Then its action reads

$$S = \int dt \int dl \left[\tfrac{1}{2}\rho \left(\frac{\partial x}{\partial t}\right)^2 - \tfrac{1}{2}\kappa \left(\frac{\partial x}{\partial l}\right)^2 - v\left(x(t,l)\right) \right] \tag{9.13}$$

where ρ is the mass density, κ is the string tension, and $v(x(t,l))$ is a potential per unit of length acting on the string.

Let us illustrate this point taking for the Lagrangian

$$L = \tfrac{1}{2} m \dot{x}^2 - V(x(t))\,. \tag{9.14}$$

Employing (9.12) we get for the Euclidean action of (9.4)

$$-\int\limits_0^{\hbar\beta} d\tau\, \mathcal{H}(x(\tau)) = -\int\limits_0^{\mathcal{T}} d\tau \left[\tfrac{1}{2} m \dot{x}^2(\tau) + V(x(\tau))\right]\,. \tag{9.15}$$

Now we take the string action (9.13) for a string *frozen* in t. The integration over t gives just the factor $\mathcal{T}$ and we have

$$S_{\text{frozen}} = -\mathcal{T} \int\limits_0^{\mathcal{L}} dl \left[\tfrac{1}{2}\kappa \left(\frac{dx}{dl}\right)^2 + v(x(l)) \right]\,. \tag{9.16}$$

Since both (9.15) and (9.16) have the same dimension (energy×time) we can, through rescaling, make them identical with exception perhaps of a multiplicative numerical constant. We do rescaling replacing

$$l = t\,\frac{l_0}{t_0} \tag{9.17}$$

where the scale l_0 has dimension of lenght and t_0 of time. Remembering that we can set $\kappa = m l_0/t_0^2$ we obtain

$$S_{\text{frozen}} = -\frac{\mathcal{T}}{t_0} \int\limits_0^{\mathcal{T}} dt \left[\tfrac{1}{2} m \left(\frac{dx}{dt}\right)^2 + l_0 v(x) \right] \tag{9.18}$$

where we can identify $l_0 v(x)$ as $V(x)$ of (9.15).

The moral of this exercise is that we can interpret (9.15) as the action of a frozen in time string (9.16) and the path integrals of nonrelativistic particles in thermal equilibrium can be represented as sums of all paths in which the dispacement x is a function of its position along the length of the string. Therefore, the state of equilibrium is devoid of time dependence, and the length of paths is inversely proportional to the temperature of the system: long paths correspond to the low- and short paths to high temperatures:

$$\mathcal{L} = \mathcal{T}\frac{l_0}{t_0} = \frac{\hbar}{k_B T}\frac{l_0}{t_0}\,. \tag{9.19}$$

All this would seem to suggest that, indeed, understanding of (9.12) needs some connection between time and space which, in our simple exercise, is provided by a string whose spatial characteristics are related to its time characteristics through a partial differential equation.

Clearly, we have the same rule of composition as for the Feynman propagators K

$$\rho(x_2, x_1, \beta) = \int dx_3\, \rho(x_2, x_3, \beta - \beta_3)\, \rho(x_3, x_1, \beta_3)\,. \tag{9.20}$$

Therefore, we can write ρ in a discretized form. Dividing $\beta\hbar$ into N segments, $\eta = \beta\hbar/N$, we have

$$\rho(x_2, x_1, \beta) = \int \prod_{i=1}^{N-1} \frac{dx_i}{a} \exp\left\{-\frac{1}{\hbar}\sum_{i=0}^{N-1} \eta \left[\frac{m}{2}\frac{(x_{i+1}-x_i)^2}{\eta^2} + V(x_i)\right]\right\} \tag{9.21}$$

where $a = \sqrt{2\pi\hbar\eta/m}$. Note that small η's correspond to high temperatures. Therefore, (9.21) tells us that we can express a density matrix for a system at a low T (large β) through density matrices at high T (small η). The second ones are, as a rule, better known than the first. Thus through discretization we can attempt to construct ρ's for very low temperatures from some well known ρ's at high temperatures.

From what we said it follows that we can have ρ in form of an operator

$$\rho = e^{-\beta H} \tag{9.22}$$

where H is the Hamilton operator. Indeed, from (9.22) we can construct the ρ in any representation we wish. For instance

$$\begin{aligned} <x_2|\rho|x_1> &= <x_2|\sum_l |\phi_l><\phi_l|e^{-\beta H}\sum_k |\phi_k><\phi_k|x_1> \\ &= \sum_l <x_2|\phi_l><\phi_l|x_1>\; e^{-\beta E_l} = \sum_l \phi_l(x_2)\phi_l^*(x_1)\, e^{-\beta E_l} \end{aligned} \tag{9.23}$$

where $\phi_l(x)$ are eigenfunctions of H: $H\phi_l(x) = E_l\phi_l(x)$. Clearly, we can multiply ρ by a unity operator $\sum_j |\psi_j><\psi_j| = 1$, where ψ_j form a complete and orthonormal set of states and use

$$\rho = \sum_j e^{-\beta H}|\psi_j><\psi_j|\,. \tag{9.24}$$

Differentiation of ρ gives

$$-\frac{\partial \rho}{\partial \beta} = H\rho\,. \tag{9.25}$$

One may use (9.25) as an operator differential equation for ρ (whose solution is given in (9.22)). We can also construct an integral equation for ρ which can be of use for construction of a perturbative expansion. To that effect let us split $H = H_0 + H_1$ where H_0 represents a simple system which we know how to solve

$$\rho = e^{-\beta H}\,, \qquad \rho_0 = e^{-\beta H_0}\,, \qquad H = H_0 + H_1\,. \tag{9.26}$$

We have

$$\frac{\partial}{\partial \beta}\left(e^{\beta H_0}\rho\right) = -e^{\beta H_0} H_1\,\rho\,. \tag{9.27}$$

We integrate both sides over β from 0 to β. Remembering that

$$\lim_{\beta\to 0}\, e^{\beta H_0}\rho\; = 1\,,$$

we find

$$e^{\beta H_0}\rho - 1\; = -\int\limits_0^\beta d\beta'\, e^{\beta' H_0} H_1\,\rho(\beta')\,,$$

hence the integral equation

$$\rho(\beta)\; =\; \rho_0(\beta) - \int\limits_0^\beta d\beta'\, e^{(\beta'-\beta)H_0} H_1\,\rho(\beta')\,. \tag{9.28}$$

This equation can generate a perturbative series (with respect to H_1) through iterations:

$$\begin{aligned}\rho(\beta)\; &=\; \rho_0(\beta) - \int\limits_0^\beta d\beta' \rho_0(\beta-\beta') H_1\,\rho_0(\beta') \\ &+ \int\limits_0^\beta d\beta' \int\limits_0^{\beta'} d\beta'' \rho_0(\beta-\beta') H_1\,\rho_0(\beta'-\beta'') H_1\,\rho_0(\beta'') + \dots\,.\end{aligned} \tag{9.29}$$

Placing unit operators, $\sum_j |j\!><\!j| = 1$, at appropriate places we can write this expansion in any representation we wish.

Another approximate procedure of relevance is the variational principle. One of the most convenient objects to subject to this procedure is the free energy, F, or the partition function, $\mathcal{Z}$. We define them through the action $S[x(\tau)]$. We have :

$$\mathcal{Z} = e^{-\beta F} = \int dx\,\rho(x,x;\beta) = \int dx(0) \int\limits_{x(\beta\hbar)=x(0)} [\mathcal{D}x(\tau)]\, e^{-\frac{1}{\hbar}S[x(\tau)]}\,. \tag{9.30}$$

The beginning $x(0)$ and the end $x(\beta\hbar)(= x(0))$ of the paths are marked as a subscript to the integral over paths. Relation (9.30) can be written as an average:

$$e^{-\beta F} = \left\langle e^{-\frac{1}{\hbar}(S-S_0)} \right\rangle_{S_0} e^{-\beta F_0} \tag{9.31}$$

where

$$\left\langle e^{-\frac{1}{\hbar}(S-S_0)} \right\rangle_{S_0} = \frac{\int dx(0) \int\limits_{x(\beta\hbar)=x(0)} [\mathcal{D}x(\tau)]\, e^{-\frac{1}{\hbar}(S-S_0)}\, e^{-\frac{1}{\hbar}S_0}}{\int dx(0) \int\limits_{x(\beta\hbar)=x(0)} [\mathcal{D}x(\tau)]\, e^{-\frac{1}{\hbar}S_0}}\,, \tag{9.32}$$

and

$$e^{-\beta F_0} = \int dx(0) \int\limits_{x(\beta\hbar)=x(0)} [\mathcal{D}x(\tau)]\, e^{-\frac{1}{\hbar}S_0}\,. \tag{9.33}$$

Clearly, S_0 is to be chosen to simplify and to make the problem which is being solved as amenable as it is possible. Let us assume, for simplicity sake, that S and S_0 are real. We can apply to (9.31) the inequality

$$\left\langle e^{-f} \right\rangle \geq e^{-\langle f \rangle}\,. \tag{9.34}$$

This inequality, the Jensen inequality (see [10.9] and also [10.6]), can be proven for real functions which are *convex* on some interval I. A function, $C(f)$, is convex on I when it satisfies the inequality

$$C(\mu f_1 + (1-\mu) f_2) \leq \mu\, C(f_1) + (1-\mu)\, C(f_2)$$

where f_1, f_2 belong to I, and $0 \leq \mu \leq 1$. One can prove that the above implies the inequality:

$$C(\sum_{i=1}^{N} \mu_i f_i) \leq \sum_{i=1}^{N} \mu_i C(f_i) \tag{9.35}$$

where $0 \leq \mu_i \leq 1$, and $\sum_{i=1}^{N} \mu_i = 1$. Leaving this proof for an exercise we note that we can take μ_i's as a probability measure and can also go to a continuum limit interpreting the summation over i as a sum over trajectories. This justifies application of (9.34) to (9.31). So, now to our exercise.

Exercise

Prove (9.35) by induction. Assuming (9.35) valid for N, we will show that it is also valid for $N+1$. Indeed, defining

$$\bar{\mu} = \sum_{i=1}^{N} \mu_i \qquad \text{and} \qquad \bar{f} = \frac{\sum_{i=1}^{N} \mu_i f_i}{\bar{\mu}}\,,$$

we write (note that $\sum_{i=1}^{N+1} \mu_i = 1$ implies $\mu_{N+1} = 1 - \sum_{i=1}^{N} \mu_i$)

$$C(\sum_{i=1}^{N+1} \mu_i f_i) = C\left(\sum_{i=1}^{N} \mu_i f_i + (1 - \sum_{i=1}^{N} \mu_i) f_{N+1}\right) = C(\bar{\mu}\bar{f} + (1-\bar{\mu}) f_{N+1})\,.$$

To this last expression we apply the definition of a convex fuction and obtain

$$C(\bar{\mu}\bar{f} + (1-\bar{\mu})f_{N+1}) \;\leq\; \bar{\mu}\, C(\bar{f}) + (1-\bar{\mu})\, C(f_{N+1})\,.$$

But we assumed (9.35), therefore

$$\bar{\mu}\, C(\bar{f}) \;\leq\; \sum_{i=1}^{N} \mu_i\, C(f_i)\,,$$

which completes the proof because

$$C(\bar{\mu}\bar{f} + (1-\bar{\mu})f_{N+1}) \;=\; C(\sum_{i=1}^{N+1} \mu_i f_i)\,.$$

End of the exercise

Now we apply (9.34) to (9.31), and obtain

$$e^{-\beta F} \;\geq\; e^{-\frac{1}{\hbar}\langle S-S_0\rangle_{S_0}}\, e^{-\beta F_0}\,, \tag{9.36}$$

hence for the exponents

$$F \;\leq\; F_0 + \frac{1}{\beta\hbar}\,\langle S-S_0\rangle\;. \tag{9.37}$$

This inequality can be employed to set up a variational procedure for finding an upper limit to the ground state energy of a system defined through S. Indeed, from (9.2) and (9.5) we can see that taking the low temperature limit ($\beta \to \infty$ in $F(\beta)$) we get

$$\lim_{\beta\to\infty} F(\beta) \;=\; \lim_{\beta\to\infty}\left[-\frac{1}{\beta}\ln \mathrm{Tr}\, e^{-\beta H}\right] \;=\; E_{\text{ground}}\,. \tag{9.38}$$

Hence, in this limit

$$E - E_0 \;\leq\; \frac{1}{\beta\hbar}\,\langle S-S_0\rangle_{S_0}\;.$$

Therefore, minimizing the r.h.s. of (9.37) through a judicious choice of S_0 (which is arbitrary!) we can approach the ground state energy as closely as our skill in choosing S_0 let us.

9.1 The Polaron Problem

When an electron moves through a polar crystal, it polarizes the medium. Hence a local polarization, a vector field $\mathbf{P}(\mathbf{x})$, is induced by the local displacements of the ions of the crystal. A local charge density, $\rho(\mathbf{x})$, results from the lattice displacements, and this charge density generates a potential, $V(\mathbf{x})$, felt by the electron. These three quantities are related through the equations

$$\Delta V(\mathbf{x}) = e\rho(\mathbf{x}) = -e\boldsymbol{\nabla}\cdot\mathbf{P}(\mathbf{x})\,. \tag{9.39}$$

The electron charge is $-e$. $\mathbf{P}$ is related to $\mathbf{E}$ and the dielectric constant which, in turn, depends on vibrations of the ions.

The crystal has vibrational modes of the lattice (phonons) and the ones which dominate the processes we are going to discuss are the modes in which the positive and negative ions move in opposite directions. It turns out that the frequencies, ω, of these modes are approximately independent on the wave vectors, $\mathbf{k}$, and $\mathbf{P}$ is parallel to $\mathbf{k}$ (longitudinal oscillations):

$$\omega(\mathbf{k}) \approx \omega \qquad \text{for all } \mathbf{k}\,. \tag{9.40}$$

Thus we expand $\mathbf{P}$ into modes

$$\mathbf{P}(\mathbf{x}) \sim \int \frac{d^3k}{(2\pi)^3} \sum_{s=1}^{3} \Big[\mathbf{E}_{\mathbf{k},s}\, a(\mathbf{k},s)\, e^{i\mathbf{k}\cdot\mathbf{x}} + \mathbf{E}^*_{\mathbf{k},s}\, a^+(\mathbf{k},s)\, e^{-i\mathbf{k}\cdot\mathbf{x}} \Big] \tag{9.41}$$

where $\mathbf{E}_{\mathbf{k},s}$ is one of three polarization vectors belonging to each $\mathbf{k}$. The charge density we get from (9.39)

$$\rho(\mathbf{x}) = -\boldsymbol{\nabla}\cdot\mathbf{P}(\mathbf{x}) \sim i \int \frac{d^3k}{(2\pi)^3} \sum_{s=1}^{3} \Big[\mathbf{k}\cdot\mathbf{E}_{\mathbf{k},s}\, a(\mathbf{k},s)\, e^{i\mathbf{k}\cdot\mathbf{x}} - \mathbf{k}\cdot\mathbf{E}^*_{\mathbf{k},s}\, a^+(\mathbf{k},s)\, e^{-i\mathbf{k}\cdot\mathbf{x}} \Big]\,.$$

Since only the longitudinal displacements contribute, $\mathbf{E}_{\mathbf{k},s}$ is paralell to $\mathbf{k}$, we have

$$\rho(\mathbf{x}) = \int \frac{d^3k}{(2\pi)^3}\, \rho(\mathbf{k})\, e^{i\mathbf{k}\cdot\mathbf{x}} \sim i \int \frac{d^3k}{(2\pi)^3}\, |\mathbf{k}| \big[a_{\mathbf{k}} e^{i\mathbf{k}\cdot\mathbf{x}} - a^+_{\mathbf{k}} e^{-i\mathbf{k}\cdot\mathbf{x}} \big] \tag{9.42}$$

where $a_{\mathbf{k}}$ are the annihilation operators for just these longitudinal modes. So, solving (9.39) for the electron potential energy due to the lattice vibrations we find the effective potential of the electron. From (9.39) $V(\mathbf{k}) = -e\rho(\mathbf{k})/k^2$, hence

$$\begin{aligned} V(\mathbf{x}) &= \int \frac{d^3k}{(2\pi)^3} \Big(-\frac{e}{k^2}\, \rho(\mathbf{k}) \Big)\, e^{i\mathbf{k}\cdot\mathbf{x}} \\ &= i \left(\sqrt{2}\pi\alpha \right)^{1/2} \int \frac{d^3k}{(2\pi)^3}\, \frac{1}{|\mathbf{k}|} \left[a^+_{\mathbf{k}}\, e^{-i\mathbf{k}\cdot\mathbf{x}} - a_{\mathbf{k}}\, e^{i\mathbf{k}\cdot\mathbf{x}} \right], \end{aligned} \tag{9.43}$$

where α is a dimensionless constant whose value varies from crystal to crystal between ~ 1 and ~ 20 (we use the same convention as in [10.4]). Assuming that $a^+_{\mathbf{k}}$ and $a_{\mathbf{k}}$ are the creation and annihilation operators of phonons we can write the complete Hamiltonian for a nonrelativistc electron moving in a vibrating lattice

$$H = \frac{\mathbf{p}^2}{2m} + \hbar\omega \int \frac{d^3k}{(2\pi)^3}\, a^+_{\mathbf{k}}\, a_{\mathbf{k}} + V(\mathbf{x})\,. \tag{9.44}$$

Here, the first term is just the kinetic energy of the electron, the second - the energy of the phonons, and the third - the electron interaction with the phonons given by (9.43). To simplify the calculations we set: $\hbar = m = \omega = 1$ (remember that ω is approximately a constant in the region of interest, compare [10.3] and

[10.4]). Note that in our Hamiltonian we do not have a zero point fluctuations of the phonons, i.e. when there are no phonons the energy of the crystal is zero.

We calculate the ground state energy of an electron of momentum p (fixed) in perturbation theory and using the variation method (from inequality (9.37)). The first perturbative calculations were done in [10.5].