Lecture 24

IRREVERSIBLE STATISTICAL MECHANICS I: HEIMS PERTURBATION THEORY

Back in Lectures 10 and 11, we saw how the principle of maximum entropy leads us to the standard Gibbs formalism of equilibrium statistical mechanics, via arguments very much shorter and simpler than the usual "ergodic" approach of antiquity. The principle is therefore, at the very least, a useful pedagogical device, by which known results may be derived more quickly. But, of course, the real test of any new principle in science is not its ability to re-derive known results, but its ability to give new results, which could not be (or at least, had not been) derived without it. Since we agree with standard formalism in all equilibrium problems, the only place where new results are possible is in the extension to nonequilibrium problems, where previously no general theory existed.

Another respect in which Lecture 11 was left incomplete, appears as soon as we try to apply that formalism to real, nontrivial physical problems; we need more powerful mathematical tools. It is one of the most satisfying things about this approach that both these needs--finding a mathematical technique for complicated equilibrium problems, and setting up a general formalism for nonequilibrium problems--are met by a single mathematical development. I'll give it in this Lecture, and we'll see its applications to equilibrium and nonequilibrium problems in the next two lectures.

24.1 Density Matrix Formulation

So far, I've worked up a formalism in which the enumeration of the possible "states of nature" could take place simply by listing all the stationary quantum states. In other words, quantities that are constants of the motion are the only things that I have allowed myself to specify so far. Evidently, if we are ever going to get to non-equilibrium theory, we have to generalize this to the case where I'm putting in information about things which are not constants of the motion, so something can happen when we let the equations of motion take over. If we started out with the initial canonical probability assignments of Lecture 11 and then solved the Schroedinger equation for the time development, we would find nothing at all happening. It would just sit there. Of course, that is as it ought to be for the equilibrium case; but for the non-equilibrium case, we need a little bit more.

Also, as just noted, even in the equilibrium case, I need to generalize this before I can actually do the calculation for non-trivial physical problems, because in practice I don't have the kind of information assumed above. The theory given so far presupposes an enumeration of the exact energy levels in my system to start with. But in a realistic problem, I can't calculate these. What we know is a Hamiltonian which, in the cases we can actually solve, can eventually be split into a term H_o which is big but simple and another term H_1 which is complicated but small,

$$H = H_o + H_1 \tag{24-1}$$

Then we have to do some kind of perturbation theory in order to find approximate values for the energy levels defined by the entire Hamiltonian. To find them exactly is a problem that we haven't solved.

It will happen in all non-trivial problems that the H_1 simply does not commute with H_o. So we have to learn how to generalize this mathematical machine so we can put in information about quantities which don't commute with each other. I can't enumerate states of nature simply by citing energy levels; in fact, I don't even know the representation in which this would be possible. For this reason, in any representation I can find, the relative phase of these quantum states has to get into the picture even for equilibrium problems. Well, we know the way to do this is to restate this theory in terms of the density matrix; let's turn to that now.

First, let's recall our basic definition of the density matrix. Again, this is perfectly standard material which is in fifty textbooks on quantum theory and statistical mechanics by now. Suppose that I have a state of knowledge about a system; and for the time being, don't worry about how I got this state of knowledge. I just want to describe it. There are various states ψ_1, ψ_2, ..., in which the system might be. I don't know which one it is. All I know is described by assigning some probability w_i to it being in the state ψ_i. Now, if I knew the system was in a definite quantum state ψ_i I could calculate the expectation value of any operator and come out with some formula like this,

$$\langle F \rangle_i = \int \psi_i^* F \psi_i \, d\tau \tag{24-2}$$

where $\int d\tau$ stands for an integration over all particle co-ordinates and, if there are spin indices in the problem, for summation over all those. Now the ψ_i functions that I started with are not necessarily orthogonal functions. They could be any old set of conceivable states of the system. But each of them could be expanded in a complete orthogonal set. Let's say that u_k are a complete orthonormal set of functions in which we can expand any state of this system. For the moment, it doesn't matter what states they are; just

any set that we know is complete. We could expand ψ_i in terms of those, getting some expansion coefficients $a_k^{(i)}$:

$$\psi_i = \sum_k u_k \, a_k^{(i)}$$

and then write

$$\langle F \rangle_i = \int \left(\sum_k u_k^* \, a_k^{(i)*} \right) F \left(\sum_j u_j \, a_j^{(i)} \right) d\tau \quad . \tag{24-4}$$

Now the a_k^* and a_j are constants which can be taken outside,

$$\langle F \rangle_i = \sum_{kj} a_k^{*(i)} \, a_j^{(i)} \int u_k^* \, F \, u_j \, d\tau \tag{24-5}$$

and the integral (or sum)

$$\int u_k^* \, F \, u_j \, d\tau = F_{kj} \tag{24-6}$$

defines the matrix element F_{kj}, in the u_k representation, so that

$$\langle F \rangle_i = \sum_{kj} F_{kj} \, a_k^{(i)*} \, a_j^{(i)} \quad . \tag{24-7}$$

The expectation value of any quantity, if I am given the wave function ψ_i, is a quadratic form in these matrix elements F_{kj}. Now if I'm in this fix where I don't know what the state is, the best expectation value I can give you is not just one of these, but I have to average it also over these w_i which represent my uncertainty as to what the actual state is,

$$\langle F \rangle = \sum_i w_i \langle F \rangle_i = \sum_i w_i \sum_{jk} F_{kj} \, a_k^{(i)*} \, a_j^{(i)} \quad . \tag{24-8}$$

Our expectation values are now double averages. Even if I knew the exact quantum state, there are still statistical things in quantum theory (or, to put it more cautiously, in the current "Copenhagen" interpretation of that theory), which would allow me to give only expectation values in general. I'm not even that well off. I don't even know what the right state is, so I have to average over that ignorance (w_i) also.

When you have a thing like (24-8), the only thing you can possibly do with it is change the order of summations and see what happens. Let me do that;

$$\langle F \rangle = \sum_{jk} F_{kj} \sum_i w_i \, a_k^{(i)*} \, a_j^{(i)} \quad .$$

Now, define a matrix ρ by

$$\sum_i w_i \, a_k^{(i)*} \, a_j^{(i)} = \rho_{jk} \tag{24-9}$$

then

$$\langle F \rangle = \sum_{jk} F_{kj} \, \rho_{jk} \quad . \tag{24-10}$$

The summation over j builds me the matrix product of $F\rho$; and then the summation over k is the sum of the diagonal elements, which we call the trace. Or, I could have written the sum with ρ and F interchanged. In this case I would now say the summation over k builds me the matrix product ρF, and then the summation over j gives the trace, so I could write this equally well as

$$\langle F \rangle = \sum_{jk} F_{kj} \, \rho_{jk} = \mathrm{Tr}(F\rho) = \mathrm{Tr}(\rho F) \quad . \tag{24-11}$$

This matrix ρ is, of course, called the density matrix, and you see that it is a Hermitian matrix,

$$\rho^*_{kj} = \rho_{jk} \quad ,$$

or in matrix notation

$$\rho^\dagger = \rho \quad . \tag{24-12}$$

The neat way to develop our quantum statistics, so the phases are taken into account automatically, is in terms of the density matrix. From now on I will express expectation values of any quantities I want to talk about in the form (24-11). We started out with a problem of how you set up a probability assignment which describes a certain state of knowledge; now we've got the problem of setting up a density matrix which describes a certain state of knowledge. Take a specific case; suppose somebody measures the total magnetic moment of some spin system and they give me a number M. I want to find a density matrix which describes what I know about this spin system when you give me just this number; or rather these three numbers, the three components $\{M_x, M_y, M_z\}$. At the very least I want my density matrix to satisfy

$$\vec{M} = \langle \vec{M}_{op} \rangle = \mathrm{Tr}\left(\rho \vec{M}_{op}\right) \quad . \tag{24-13}$$

In other words, if I give this density matrix to anybody else, and he tries to predict the moments from the density matrix, he should be able to get back the numbers that were given to me, by following the usual rule for prediction in statistical mechanics. If he couldn't do that, then it wouldn't make sense to say that the density matrix "contained" the given information $\{M_x, M_y, M_z\}$. This is all we are doing when we choose ρ to satisfy (24-13).

In general, there are an infinite number of density matrices which would all do this. Again, I am faced with the problem of making a free choice of a density matrix, which is "honest" in the sense that it doesn't assume things that I don't know, and spreads out the probability as evenly as possible over all possibilities allowed by what I do know. Well, we started out with

$$S_I = -\sum_i p_i \log p_i$$

so, suppose we now take

$$S_A = -\sum_i w_i \log w_i \qquad (24\text{-}14)$$

and we might choose the density matrix which makes S_A a maximum. If we took that as our measure of amount of uncertainty, we would be in a little bit of trouble. A sort of Gibbs paradox would show up. I said that these initial states ψ_i that we started out with are not necessarily orthogonal to each other. In fact, I can have state ψ_1 and I give it a probability w_1; to the state ψ_2 I give probability w_2. Now, let's make a continuous change in the problem such that $\psi_2 \Longrightarrow \psi_1$; my state of knowledge shades continuously into: ψ_1 with a probability (w_1+w_2). But nothing like that happens to S_A. In S_A as $\psi_2 \Longrightarrow \psi_1$ the term $-w_1 \log w_1 - w_2 \log w_2$ would have to be replaced suddenly by

$$-(w_1+w_2)\log(w_1+w_2) \quad .$$

If we took this quantity S_A as the measure of uncertainty about the system, then you would have this phenomenon of sudden discontinuities in my uncertainty when two wave functions suddenly become exactly equal. But my intuitive state of knowledge has no discontinuity when I do that. It goes continuously from one case to another. That's one thing that would be wrong if I tried to use this S_A as my measure of uncertainty.

There's another thing that would be even worse, and perhaps easier to see. For a given density matrix, there's no upper limit to the S_A that I could get. If S_A is going to be the thing that counts, I'll say I've got 26 different states, ψ_a to ψ_z. They all happen to be equal to ψ_1 but I assign probabilities w_a to w_z to them. Now, of course, my summation

$$-\sum_{a=1}^{26} w_a \log w_a$$

over the alphabet--my notation is not quite consistent, but I think you see the point--my summation over all these terms could be a very large number. I can introduce thousands of them. There would be no upper limit to the $-\sum w \log w$ I could get if I used this S_A.

On the other hand, there's one property that is unique. S_A has no upper bound. S_A does have a lower bound. S_A for a given density matrix has an absolute minimum given by

$$S_A \geq -\mathrm{Tr}(\rho \log \rho) \ . \qquad (24\text{-}15)$$

There's one and only only one way, in general, of setting up these states ψ_i and corresponding probabilities w_i so that this lower bound is reached. When I say "in general," I mean if there are no degeneracies in the eigenvalues of ρ. I think that I will not bother to give you the proof of this. The proof is given in this second paper that I had a long time ago [Physical Review 108, 171, (1957)].

Well, now what does $\log \rho$ mean? I have to do that for the next step. ρ is a Hermitian matrix and there's a theorem in matrix theory that says, there is a matrix S such that

$$S\rho S^{-1} = \begin{pmatrix} \rho_1 & & & \\ & \rho_2 & & \\ & & \ddots & \\ & & & \rho_n \end{pmatrix} \qquad (24\text{-}16)$$

I can always find some similarity transformation which would have made this diagonal. Now, in the representation where ρ is diagonal, then by $\log \rho$ I mean the diagonal matrix

$$\log \rho = \begin{pmatrix} \log \rho_1 & & & \\ & \log \rho_2 & & \\ & & \ddots & \\ & & & \log \rho_n \end{pmatrix} \qquad (24\text{-}17)$$

If I choose for my basis u_k the particular set of functions ψ_i for which S_A does reach its absolute minimum value, then the diagonal elements of ρ are just the probabilities w_i assigned to these states. In other words, the choice of possible states ψ_i which makes S_A a minimum for a given ρ, is the one for which the probabilities w_i assigned to these states are the eigenvalues of this matrix ρ.

The reason we had a Gibbs paradox at the beginning here was that I said these different states ψ_i that I'm taking into account are not necessarily orthogonal. If states ψ_1 and ψ_2 are not orghogonal and you tell me the system is in state ψ_1, then, of course, the present Copenhagen interpretation says: the probability that, if I did a measurement, I would actually find it in ψ_2, is not zero. It's the scalar product squared, $|(\psi_1,\psi_2)|^2$; sometimes called the transition probability from one state to another. I'm not writing down the probabilities of mutually exclusive events unless I choose my states ψ_i to be orthogonal, and that's just what I do by making the choice that

minimize S_A. I'm going to say now that the S_I for a density matrix is this unique minimum value of S_A:

$$S_I \equiv -\mathrm{Tr}(\rho \log \rho) \tag{24-18}$$

There are a number of other arguments why you choose (24-18) rather than some other expressions that you could think of, and they are also given in this previously mentioned paper. I want not to show you some examples of equilibrium statistical mechanics using this and I want to develop a general perturbation theory in which, if there's a complicated problem I can break it down into a simple problem plus a small change. I want to learn how to expand this density in powers of some small perturbation and the perturbation theory we get will also be exactly the one we need for our irreversible theory tomorrow. Now, we are back at the same problem that we studied in Lecture 10, but the $\langle F_k \rangle$ are matrices, and the constraints are

$$\langle F \rangle_k = \mathrm{Tr}(\rho F_k), \quad k = 1, 2, \ldots, m \quad . \tag{24-19}$$

This restricts my density matrix. I must find which density matrix will maximize S_I while agreeing with conditions we have imposed on it. Now, the formal solution of this goes through in exactly the same way as we did in Lecture 10. In fact, you recall that my proof back then was based on the fact that when I have an ordinary discrete probability distribution

$$\sum_{i=1}^{n} p_i \log p_i \geq \sum_{i=1}^{n} p_i \log u_i \tag{24-20}$$

the inequality becomes an equality if, and only if, $p_i = u_i$. Now, we have a precisely similar situation here. You can prove that if ρ and σ are any two density matrices, there is an inequality

$$\mathrm{Tr}\{\rho \log \rho\} \geq \mathrm{Tr}\{\rho \log \sigma\} \tag{24-21}$$

I'll leave this as an "exercise for the reader" to prove. The argument goes through precisely the way I did it before. The solution to this problem was given long ago by von Neumann (Göttinger Nachrichten, 1927).

The mathematical properties that I am talking about have been well known for a long time; but the new viewpoint about the <u>significance</u> of those properties is the thing that I'm selling here. These properties provide the justification for choosing certain distributions in preference to certain other ones. The density matrix that maximizes S_I subject to these constraints is again given by

$$\rho = \frac{1}{Z(\lambda_1 \cdots \lambda_m)} \exp\left\{-\lambda_1 F_1 - \cdots \cdots - \lambda_m F_m\right\} \tag{24-22}$$

One would guess, of course, that it generalizes in some such way as this, but I don't think your intuition would tell you whether the proper generalization was exactly this form. All the formal properties that I wrote down this morning follow from this distribution just the same way that we gave before with one exception, which I'll get to after we've developed our mathematics a little bit more.

Of course the number one must have expectation value of one,

$$\langle 1 \rangle = \mathrm{Tr}(\rho 1) = \mathrm{Tr}(\rho) \quad . \tag{24-23}$$

This is one more condition just like the one this morning that p_i had to be equal to one. The normalizing factor which will guarantee that the trace of this thing is one, is evidently

$$Z(\lambda_1 \ldots\ldots \lambda_m) = \mathrm{Tr}\ \exp\left\{-\lambda_1 F_1 - \ldots\ldots - \lambda_m F_m\right\} \tag{24-24}$$

which is the partition function.

Now perhaps I ought to say a word about what is meant by the exponential of a matrix. If I have any function of an ordinary number x that I can expand in a power series,

$$f(x) = \sum_{n=0}^{\infty} a_n\, x^n \quad , \tag{24-25}$$

of course, there is nothing to stop me from defining the same function of a matrix by the same power series,

$$f(M) = \sum_{n=0}^{\infty} a_n\, M^n \quad . \tag{24-26}$$

Then the question arises; does this converge to a definite matrix and if so does the resultin matrix f(M) have any useful properties? There is a theorem: if the original power series converged for x equal to each of the eigenvalues of the matrix M, then the power series is guaranteed to converge to a definite matrix f(M). Now in particular the exponential function,

$$e^x = \sum_{n=0}^{\infty} \frac{x^n}{n!} \tag{24-27}$$

converges so well it has infinite radius of convergence and, therefore, the exponential of any square matrix with finite elements is guaranteed to exist and to be a well defined matrix.

The choosing of the λ_k is again something which we do in order to make the expectation values agree with the given data. Again it's going to turn out that same formal relations hold when we are talking matrices. Again we have to solve

$$\langle F_k \rangle = -\frac{\partial}{\partial \lambda_k} \log Z \tag{24-28}$$

for the λ_k. But to prove that this is right, we have to give a mathematical argument that is a little more involved than that needed to prove (It turns out that this argument is also fundamental to everything that I want to talk about from now on, so let's take time out for it now.

24.2 Heims Perturbation Theory

I would like to develop what I call the Heims' perturbation theory. This was worked out in about 1959 by my former student, Steve Heims, and we published a very truncated account of it in the appendix to a paper on gyromagnetic effects [Revs. Mod. Physics 34, 143 (1962)]. You see we have always the problem of evaluating exponentials of matrices. First, I would like to work out the well-known perturbation expansion of this. I have a matrix A, and the matrix e^A is something that I can do. That is simple. But the thing I really want to evaluate is

$$e^{(A+\text{something else})}$$

or

$$e^{A+\varepsilon B} = e^A\left[1 + \sum_{n=1}^{\infty} \varepsilon^n S_n\right] \quad . \tag{24-29}$$

And I will indicate that this something else is small by putting ε in it and expanding in powers of ε. You see this is the typical situation we would have if we tried to evaluate a density matrix

$$\rho = \frac{1}{Z} \exp\left\{-\lambda_1 F_1 - \lambda_2 F_2 - \cdots - \lambda_m F_m\right\} \quad . \tag{24-30}$$

Some of these operators might be simple so I could evaluate their exponentials; then some others might be complicated and not commute with the others, and they would mess up the whole problem. At that point I would resort to approximations. To put it in general form, let's talk just A and B for a while.

Let me form a quantity

$$e^{-xA}\, e^{x(A+\varepsilon B)}$$

where x is an ordinary number and by xA I mean the matrix in which every element is multiplied by x. If I let ε go to zero, this goes into the unit matrix. But it isn't quite the unit matrix, if ε is not zero. But how does it vary with x? Well, by staring at this power series definition of the exponential function, you can convince yourself very quickly that the same rule for differentiating an exponential function works even if a matrix is in the exponent. I have my choice of writing it either way:

$$\frac{d}{dx}e^{-xA} = -Ae^{-xA} = -e^{-xA}\, A \qquad . \tag{24-31}$$

Therefore,

$$\frac{d}{dx}\left[e^{-xA}e^{x(A+\varepsilon B)}\right] = -e^{-xA}\, Ae^{x(A+\varepsilon B)} + e^{-xA}(A+\varepsilon B)e^{x(A+\varepsilon B)} \tag{24-32}$$

Now two terms cancel, and ε is just a number, so

$$\frac{d}{dx}\left[e^{-xA}e^{x(A+\varepsilon B)}\right] = e^{-xA}\, Be^{x(A+\varepsilon B)} \qquad . \tag{24-33}$$

I can't pull that B outside because in general it doesn't commute with what is either to the left of it or to the right of it. Now that I've differentiated this thing, let me integrate with respect to x and get it back again:

$$\int_0^x \frac{d}{dx_1}\left[e^{-x_1A}\, e^{x_1(A+\varepsilon B)}\right]dx_1 = e^{-xA}e^{x(A+\varepsilon B)} - I$$

$$= \varepsilon\int_0^x e^{-x_1A}\, Be^{x_1(A+\varepsilon B)}\, dx_1 \qquad . \tag{24-34}$$

Now let me clean this up. Multiplying both sides by e^{xA} from the left, we find

$$e^{x(A+\varepsilon B)} = e^{xA}\left[1 + \varepsilon\int_0^x e^{-x_1 A}\, B e^{x(A+\varepsilon B)}\, dx_1\right]. \qquad (24\text{-}35)$$

This is an integral equation which $e^{x(A+\varepsilon B)}$ satisfies. Well now, if you have an integral equation, you grind out perturbation solutions of it simply by iteration--i.e., substituting the equation into itself over and over again. So, let me write this in still easier form,

$$e^{x(A+\varepsilon B)} = e^{xA}\left[1 + \varepsilon\int_0^x e^{-x_1 A}\, B e^{x_1(A+\varepsilon B)}\, dx_1\right] \quad . \qquad (24\text{-}36)$$

The first iteration gives

$$e^{x(A+\varepsilon B)} = e^{xA}\left\{1 + \varepsilon\int_0^x dx_1 e^{-x_1 A}\, B e^{x_1 A}\left[1 + \varepsilon\int_0^{x_1} dx_2 e^{-x_2 A}\, B e^{x_2(A+\varepsilon B)}\right]\right\}$$

$$= e^{xA}\left\{1 + \varepsilon\int_0^x dx_1 e^{-x_1 A}\, B e^{x_1 A} + \varepsilon^2\int_0^x dx_1\int_0^{x_1} dx_2 e^{-x_1 A}\, B e^{(x_1-x_2)A}\, B e^{x_2(A+\varepsilon B)}\right\},$$

and by repeated substitution we get

$$e^{A+\varepsilon B} = e^{A}\left[1 + \varepsilon\int_0^1 e^{-xA}\, B e^{xA}\, dx + \right.$$

$$\varepsilon^2\int_0^1 dx_1\int_0^{x_1} dx_2 e^{-x_1 A}\, B e^{(x_1-x_2)A}\, B e^{x_2 A} +$$

$$\left. B e^{(x_2-x_3)A}\, B e^{x_3 A} + \ldots\right] \varepsilon^3\int_0^1 dx_1\int_0^{x_1} dx_2\int_0^{x_2} dx_3 e^{-x_1 A}\, B e^{(x_1-x_2)A} \quad . \qquad (24\text{-}37)$$

We can keep playing this game as long as we please, and so this generates an infinite series in powers of ε. Or, we can terminate (24-37) at any finite number of terms, replace A by A + εB in the last exponent, and it is an exact equation. The exponential of any matrix is a well-behaved thing, so

we can put in any ε we please--large or small-- and the infinite series is guaranteed to converge to the right thing. Of course, if we have to take more than about two terms of the series, then we'll be wound up in another bad calculation and this whole method will not be too useful.

Let's summarize this: we have found the power series expansion

$$e^{A+\varepsilon B} = e^{A}\left[1 + \sum_{n=1}^{\infty} \varepsilon^{n} S_{n}\right] \tag{24-38}$$

in which

$$S_1 \equiv \int_0^1 e^{-xA} B e^{xA} dx \tag{24-39}$$

$$S_2 \equiv \int_0^1 dx_1 \int_0^{x_1} dx_2 \; e^{-x_1 A} B e^{(x_1 - x_2)} B e^{x_2 A} \tag{24-40}$$

and if we write

$$B(x) \equiv e^{-xA} B e^{xA} \tag{24-41}$$

the general order term is

$$S_n \equiv \int_0^1 dx_1 \int_0^{x_1} dx_2 \cdots \int_0^{x_{n-1}} dx_n \; B(x_1)B(x_2)\cdots B(x_n) \quad . \tag{24-42}$$

Now we have an "unperturbed" density matrix

$$\rho_o = \frac{e^{A}}{Tr\left(e^{A}\right)} \tag{24-43}$$

and a "perturbed" one:

$$\rho = \frac{e^{A+\varepsilon B}}{Tr\left[e^{A+\varepsilon B}\right]} \tag{24-44}$$

In the unperturbed ensemble, any particular operator C has the expectation value

$$\langle C\rangle_o = \mathrm{Tr}(\rho_o C) \tag{24-45}$$

and in the perturbed ensemble, it will be instead,

$$\langle C\rangle = \mathrm{Tr}(\rho C) \quad . \tag{24-46}$$

And what I would really like to get is a power series expansion of <C>. So let's write out the expansion we would like to get; using (24-38),

$$\langle C\rangle = \frac{\mathrm{Tr}\left[e^{A+\varepsilon B}C\right]}{\mathrm{Tr}\left[e^{A+\varepsilon B}\right]} = \frac{\mathrm{Tr}\left(e^{A}C\right) + \sum_{n=1}^{\infty} \varepsilon^n \mathrm{Tr}\left(e^{A}S_n C\right)}{\mathrm{Tr}\left(e^{A}\right) + \sum_{i=1}^{\infty} \varepsilon^n \mathrm{Tr}\left(e^{A}S_n\right)}$$

and divide by $\mathrm{Tr}\left(e^{A}\right)$ to get, from (24-45),

$$\langle C\rangle = \frac{\langle C\rangle_o + \sum_{n=1}^{\infty} \varepsilon^n \langle S_n C\rangle_o}{1 + \sum_{n=1}^{\infty} \varepsilon^n \langle S_n\rangle_o} \tag{24-47}$$

I've got everything reduced to expectation values calculated in the unperturbed distribution, which I assumed was something simple that I could calculate. But still this is in a little messy form. I've got the ratio of two infinite series--I know they are well-behaved series. Both the numerator and denominator series have infinite radius of convergence. But, I would like to write this as a single series over ε and get rid of this denominator. If I can invert the power series for this denominator; that is, find the coefficients a_n in

$$\frac{1}{1 + \sum_{n=1}^{\infty} \varepsilon^n \langle S_n\rangle_o} = 1 - \sum_{n=1}^{\infty} a_n \varepsilon^n \quad ,$$

then we'll have it. This equation is the same as

$$1 = \left(1 + \sum_{n=1}^{\infty} \varepsilon^n \langle S_n \rangle_o\right)\left(1 - \sum_{n=1}^{\infty} \varepsilon^m a_m\right)$$

or

$$1 = 1 + \sum_{n=1}^{\infty} \varepsilon^n \left[\langle S_n \rangle_o - a_n - \sum_{k=1}^{n-1} \langle S_k \rangle_o \, a_{n-k}\right] \quad .$$

Now if a power series in ε is to vanish identically (i.e., for all ε), the coefficient of each term must be zero. So, my problem is: choose the a_n so that

$$\langle S_n \rangle_o = a_n + \sum_{k=1}^{n-1} \langle S_k \rangle_o \, a_{n-k} \quad . \tag{24-48}$$

This is a discrete version of a Volterra integral equation, and is solved as follows. Define a sequence of operators Q_n,

$$Q_1 \equiv S_1 \tag{24-49}$$

$$Q_2 \equiv S_2 - S_1 \langle Q_1 \rangle_o \tag{24-50}$$

$$Q_n \equiv S_n - \sum_{k=1}^{n-1} S_k \langle Q_{n-k} \rangle_o \quad , \quad n > 1 \tag{24-51}$$

Taking the expectation value of (20-51) and comparing with (24-48), you see that the desired solution is just

$$a_n = \langle Q_n \rangle_o \tag{24-52}$$

Now, returning to (24-47) with this result, we have

$$\langle C \rangle = \left[\langle C \rangle_o + \sum_{k=1}^{\infty} \varepsilon^k \langle S_k C \rangle_o\right]\left[1 - \sum_{m=1}^{\infty} \varepsilon^m \langle Q_n \rangle_o\right] \quad . \tag{24-53}$$

In expanding this, note that the double sum can be written as

$$\sum_{k=1}^{\infty}\sum_{m=1}^{\infty}\varepsilon^{k+m}\langle S_k C\rangle_o\langle Q_n\rangle_o = \sum_{n=2}^{\infty}\varepsilon^n\sum_{k=1}^{n-1}\langle S_k C\rangle_o\langle Q_{n-k}\rangle_o \qquad (24\text{-}54)$$

and we might as well add the term with n=1, since it vanishes anyway, having no terms at all. So, we have

$$\langle C\rangle = \langle C\rangle_o + \sum_{n=1}^{\infty}\varepsilon^n\langle S_n C\rangle_o - \sum_{k=1}^{n-1}\langle S_k C\rangle_o\langle Q_{n-k}\rangle_o - \langle Q_n\rangle_o\langle C\rangle_o \qquad (24\text{-}55)$$

and, comparing with (24-51), we get a pleasant surprise; patience and virtue are rewarded at last with what we had no right to expect in such a problem; a neat and simple final result:

$$\langle C\rangle - \langle C\rangle_o = \sum_{n=1}^{\infty}\varepsilon^n\left[\langle Q_n C\rangle_o - \langle Q_n\rangle_o\langle C\rangle_o\right] \quad . \qquad (24\text{-}56)$$

The n'th order contribution to <C> is just the covariance, in the unperturbed ensemble, of Q_n with C. The first-order term in (24-56) has long been known; to the best of my knowledge, Steve Heims was the first person to see that it can be extended to all orders. In several years of living with this formula, and seeing what it can do for us, I have come to regard it as easily the most important general rule of statistical mechanics; almost every "useful" calculation in the field can be seen as a special case of it.

So, this is the general perturbation expansion that we'll use. Every calculation I do from now on will be a special case of the application of Heims' theorem (24-56). Now, the first order correction of course is always the most important one. The first order term has a symmetry property which follows from this cyclic property of the trace, Eq. (24-11); and let me just

show that to you. To first order, since $O_1 = S_1$, I have simply

$$\langle C\rangle - \langle C\rangle_o = \varepsilon\left[\langle S_1 C\rangle_o - \langle S_1\rangle_o\langle C\rangle_o\right] \tag{24-57}$$

but

$$S_1 \equiv \int_o^1 e^{-xA}\, B e^{xA}\, dx$$

so that

$$\langle S_1\rangle_o = \int_o^1 dx \langle e^{-xA}\, B e^{xA}\rangle$$

$$= \frac{\int_o^1 dx\ \mathrm{Tr}\left[e^{(1-x)A}\, B e^{xA}\right]}{\mathrm{Tr}\left(e^{A}\right)} \quad . \tag{24-58}$$

Now, as in (24-11), it is true generally that $\mathrm{Tr}(FG) = \mathrm{Tr}(GF)$; and so

$$\langle S_1\rangle_o = \frac{\int_o^1 dx\ \mathrm{Tr}\left[e^{xA}\, e^{(1-x)A}\, B\right]}{\mathrm{Tr}\left(e^{A}\right)} = \frac{\mathrm{Tr}\left(e^{A} B\right)}{\mathrm{Tr}\left(e^{A}\right)} = \langle B\rangle_o \quad , \tag{24-59}$$

so the first-order correction always reduces to

$$\langle C\rangle - \langle C\rangle_o = \varepsilon\left[\int_o^1 dx \langle e^{-xA}\, B e^{xA} C\rangle_o - \langle B\rangle_o\langle C\rangle_o\right] \quad . \tag{24-60}$$

[At this point, we can verify Eq. (24-28). Make the choices $A = -\lambda_1 F_1 - \ldots - \lambda_m F_m$, $\varepsilon B = -\delta\lambda_k F_k$. Then $Z(\lambda_1 \ldots \lambda_m) = \mathrm{Tr}\left(e^{A}\right)$ and from the definition of a derivative,

$$\frac{\partial \log Z}{\partial\, \lambda_k} = \frac{1}{Z} \lim_{\delta\lambda_k \to o} \frac{Z\left[\lambda_1 \ldots \lambda_k + \delta\lambda_k \ldots \lambda_m\right] - Z\left[\lambda_1 \ldots \lambda_k \ldots \lambda_m\right]}{\delta\lambda_k} \quad . \tag{24-61}$$

In the limit $\delta\lambda_k \to 0$, only the first-order term survives, and so

$$\frac{\partial \log Z}{\partial \lambda_k} = \frac{\mathrm{Tr}\left(e^A S_1\right)}{Z \delta \lambda_k} = \frac{\langle S_1 \rangle_o}{\delta \lambda_k} \quad . \tag{24-63}$$

But, using (24-59), you see that this is just (24-28)].

Now I want to show you a very important symmetry property; if I interchange B and C in the right-hand side of (24-60), I don't change it. The last term I have worked into a form where it is obvious. We still have to play with the first one a little bit. Again, let's write this as the ratio of two traces.

$$\int_o^1 dx \langle e^{-xA} B^{xA} C \rangle_o = \frac{\int_o^1 dx \, \mathrm{Tr}\left[e^{(1-x)A} B e^{xA} C\right]}{\mathrm{Tr}\left(e^A\right)} \tag{24-64}$$

This time I choose to interchange matrices as follows,

$$\int_o^1 dx \, \mathrm{Tr}\, e^{(1-x)A} B e^{xA} C = \int_o^1 dx \, \mathrm{Tr}\left[e^{xA} C e^{(1-x)A} B\right] \quad . \tag{24-65}$$

Now for any $f(x)$, we have

$$\int_o^1 f(x)dx = \int_o^1 f(1-x)dx \tag{24-66}$$

consequently we can write (24-65) as

$$\int_o^1 dx \, \mathrm{Tr}\left[e^{(1-x)A} C e^{xA} B\right] \quad , \tag{24-67}$$

and writing this back as an expectation

$$\int_o^1 dx \langle e^{-xA} B e^{xA} C \rangle_o = \int_o^1 dx \langle e^{-xA} C e^{xA} B \rangle_o \quad . \tag{24-68}$$

After all this, the only thing that has happened is that I've interchanged B and C.

Now this is a very important symmetry property. If I perturb my density matrix by adding in formation about B and I calculate what effect that makes on my prediction of C, it is the same as if I had perturbed my density matrix by putting in information about C and calculated what effect that makes on B. In the next Lecture, I'll show you a whole string of physical reciprocity laws that come out of (24-68).

Again, I'm leaving you on a note where we have an enormous amount of abstract stuff and you haven't seen the physical problem. In the next two Lectures, we'll make up for that.