

Linear Response Theory and Kubo Formulas

I. SUSCEPTIBILITY

The relation $\delta\langle M \rangle = \langle M \rangle - M_0 = \chi H$ relates a response $\delta\langle M \rangle$ to an applied external field H . In case there is a magnetization $\langle M \rangle = M_0$ in zero applied field, this has been subtracted out. This defines a linear response coefficient χ . Since the complete response will always have some non-linear behavior at high fields H , it is necessary to remember that χ is defined in the limit of a small applied field ($\chi = \partial\langle M \rangle / \partial H$.) It is also assumed that the system is held close to thermal equilibrium at temperature T by a heat bath.

We now generalize this definition to a general sort of response to an arbitrary sort of field. Let the field be denoted by $F(\vec{r}, t)$ and the response be some measurable property $p(r)$ which is the expectation value of an operator $\hat{p}(r)$. The general linear relation between $p(r)$ and F is

$$\delta\langle \hat{p}(\vec{r}, t) \rangle = \int d\vec{r}' \int_{-\infty}^t \chi(\vec{r}, \vec{r}'; t - t') F(\vec{r}', t'). \quad (1)$$

Note that the response in general can be non-local in space and in time. The range in time over which the system “remembers” the earlier external perturbation is the characteristic relaxation or thermalization time τ . (Hydrodynamic effects can cause long-time “tails” in the response function, but these are usually unimportant for transport properties of solids.) The spatial range is the characteristic particle mean free path or thermalization length ℓ . (Long-range particle interactions are usually not important either.)

To simplify the notation, let us temporarily consider the special case of a spatially homogeneous applied field $F(t)$, and study the property P which is $p(r)$ spatially averaged over the volume V of the system.

$$\hat{P} \equiv \frac{1}{V} \int d\vec{r} \hat{p}(\vec{r}) \quad (2)$$

$$\delta\langle \hat{P}(t) \rangle = \int_{-\infty}^t dt \chi(t - t') F(t') \quad (3)$$

$$\chi(t - t') = \frac{1}{V} \int d\vec{r} \int d\vec{r}' \chi(r, r'; t - t'). \quad (4)$$

Nearly all of the general results of linear response theory are statements about $\chi(t - t')$, which also apply to the more general case of $\chi(r, r'; t - t')$.

The universe has four components: the “system” under observation, the observer, the field F controlled by the observer, and the heat bath which keeps the system at equilibrium when F is not applied. The response function χ is a property of the system at temperature T , but not in general an equilibrium property; it can’t be calculated from the partition function Z , for example. However, χ

can be computed from knowledge of the ground state and excitations of the system. We shall see that it is a kind of correlation function describing fluctuations which occur in the system in equilibrium.

Before the field F is applied, there is no response. While in equilibrium, the system is invariant in time (this is the definition of equilibrium.) Therefore the response at time t can only depend on the interval $t - t'$ between the time of measurement t and the time t' at which the field acts. In general, the system is not invariant under translations in space, so χ depends separately on the point \vec{r} of measurement and the point \vec{r}' at which the field acts, and not just on the interval $\vec{r} - \vec{r}'$.

The spatial integral in Eq. (1) goes over the whole system, while the time integral goes only over times t' **before** the measurement is made. This is the fundamental property of “causality.” To be specific, suppose the field has the form of a “unit impulse”, $F(t) = \delta(t)$. The results of the rest of this section will be written for the spatially homogeneous case $\chi(t - t')$ but will also apply to the inhomogeneous case $\chi(r, r'; t - t')$. From Eq. (1), the response to this unit impulse is

$$\delta\langle\hat{P}(t)\rangle = \chi(t) \tag{5}$$

where $\chi(t)$ is defined to be zero for negative times t . In words, χ is defined as the response at time t to a unit impulse applied at time $t = 0$. It is also interesting to consider the response to an *ac* applied field

$$F(t) = F_0 e^{-i\omega t} \tag{6}$$

$$\delta\langle\hat{P}(t)\rangle \equiv \chi(\omega) F_0 e^{-i\omega t}. \tag{7}$$

This defines the frequency-dependent susceptibility, $\chi(\omega)$. From Eqs. (1,6,7) we find

$$\chi(\omega) = \chi_1 + i\chi_2 = \int_0^\infty d\tau \chi(\tau) e^{i\omega\tau}. \tag{8}$$

Thus $\chi(\omega)$ is a complex function. Any actual applied field $F(t)$ will be a real quantity, so the correct interpretation of Eq. (6) is that only the “real part” $F_0 \cos(\omega t)$ is meant. Because the response is linear, and taking the real part is a linear operation, therefore the response to the real part of the complex field $F_0 \cos(\omega t)$ is the real part of the (not actually physical) response to the complex field. This means that the correct interpretation of Eq. (7) is

$$\delta \langle \hat{P}(t) \rangle = \chi_1(\omega) F_0 \cos(\omega t) + \chi_2(\omega) F_0 \sin(\omega t). \tag{9}$$

Thus the “real” and “imaginary” parts χ_1 and χ_2 have the interpretations that χ_1 gives the “in-phase” part of the response (oscillating like $\cos(\omega t)$ as does the field) while χ_2 gives the “out-of-phase” response. It will turn out that one of these parts contains the dissipative response, and the other is “reactive.”

Causality gives an important relation between these two pieces, known as the “Kramers-Kronig” relations. First we show that causality implies that $\chi(\omega)$ as given in Eq. (8), is analytic in the upper half of the complex z plane, when considered as a function of a complex frequency z (whose real part is the physical frequency ω .) Writing $z = x + iy$ where $x = \omega$,

$$\chi_1 = \int_0^\infty d\tau \chi(\tau) e^{-y\tau} \cos(x\tau) \tag{10}$$

$$\chi_2 = \int_0^\infty d\tau \chi(\tau) e^{-y\tau} \sin(x\tau). \tag{11}$$

The Cauchy relations are necessary and sufficient conditions for a function to be analytic, and are clearly satisfied by Eqs. (10,11):

$$d\chi_1/dx = d\chi_2/dy \quad (12)$$

$$d\chi_2/dx = -d\chi_1/dy. \quad (13)$$

To prove that Eqs. (12,13) follow from (10,11) it is necessary to interchange the operations of differentiation and integration, which is permitted only if the integrals are absolutely convergent. This property clearly holds only when $y > 0$, i.e. in the upper half z plane. Also it is clear that if χ had not been causal, that is, if $\chi(\tau)$ had been non-zero for negative as well as positive times τ , then analyticity would not have been established anywhere. The fact that it is the **upper** rather than the lower half of the complex frequency plane where χ is analytic follows from an arbitrary sign convention introduced in Eq. (6), namely that the external field oscillates as $e^{-i\omega t}$ rather than as $e^{+i\omega t}$. The two choices are equally sensible, so it is necessary to choose a convention and stick with it.

The Kramers-Kronig relations are valid for any function which is analytic in the upper half plane and vanishes as $|z| \rightarrow \infty$. Cauchy's theorem gives the identity

$$0 = \oint_C dz \frac{\chi(z)}{z - \omega} \quad (14)$$

where C denotes the contour shown in fig.1.

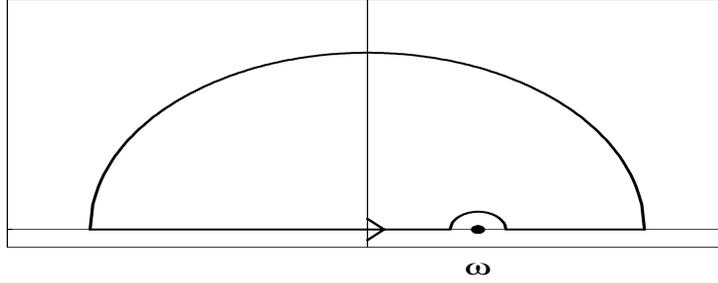


Figure 1 The contour C used in Eq. (14)

Because χ vanishes as $|z|$ goes to infinity, the large arc of C contributes nothing as it recedes to infinity. The remaining part of the contour can be separated into the straight part, which becomes a principle-value integral as the small arc shrinks, and an integral over the small arc which is parameterized by $z = \omega + \epsilon e^{i\phi}$. Thus Eq. (14) becomes

$$0 = P \int_{-\infty}^{\infty} d\omega' \frac{\chi(\omega')}{\omega' - \omega} + \lim_{\epsilon \rightarrow 0} \int_{\pi}^0 \frac{i\epsilon e^{i\phi} d\phi}{\epsilon e^{i\phi}} \chi(\omega + \epsilon e^{i\phi}). \quad (15)$$

This becomes the general relation

$$\chi(\omega) = \frac{P}{i\pi} \int_{-\infty}^{\infty} d\omega' \frac{\chi(\omega')}{\omega' - \omega}. \quad (16)$$

Finally, separating into real and imaginary parts and using the results from Eqs. (10,11) that χ_1 is even in ω and χ_2 is odd, this becomes

$$\chi_1(\omega) = \frac{2P}{\pi} \int_0^{\infty} d\omega' \frac{\omega' \chi_2(\omega')}{\omega'^2 - \omega^2} \quad (17)$$

$$\chi_2(\omega) = -\frac{2\omega P}{\pi} \int_0^{\infty} d\omega' \frac{\chi_1(\omega')}{\omega'^2 - \omega^2}. \quad (18)$$

II. MECHANICAL PERTURBATIONS

Let the system be described by the Hamiltonian

$$H = H_0 - \hat{Q}F_0e^{-i(\omega+i\eta)t} \equiv H_0 + H'(t) \quad (19)$$

where H_0 describes the “system” and F_0 is the amplitude of the applied field as described above. It is assumed that this field is coupled linearly to the system through some operator of the system denoted by \hat{Q} . The frequency ω is given an infinitesimal positive imaginary part η , such that the field is “off” at $t = -\infty$ and gradually turns on as t increases. At $t = -\infty$ the system is in thermal equilibrium, and is therefore described by a density matrix $\rho = \rho_0$ given by

$$\rho_0 = \frac{1}{Z}e^{-\beta H_0} \quad (20)$$

where β is the inverse temperature $1/k_B T$ and Z is the partition function $Z = \text{tr} \exp(-\beta H_0)$.

To follow the evolution of the system as the temperature evolves, we can integrate the Liouville equation,

$$i\frac{\partial \rho}{\partial t} = [H(t), \rho(t)] \quad (21)$$

which can be written in integrated form as

$$e^{iH_0 t} \rho(t) e^{-iH_0 t} = \rho_0 - i \int_{-\infty}^t d\tau e^{iH_0 \tau} [H'(\tau), \rho(\tau)] e^{-iH_0 \tau} \quad (22)$$

This can be solved by iteration in powers of the perturbation H' . We are interested in the response only to first order in H' , so iterating to first order we get

$$\rho(t) = \rho_0 + \delta\rho F_0 e^{-i(\omega+i\eta)t} \quad (23)$$

$$\delta\rho = i \int_0^\infty dt' e^{-iH_0 t'} [\hat{Q}, \rho_0] e^{+iH_0 t'} e^{i(\omega+i\eta)t'}. \quad (24)$$

Using this formula we can calculate the evolution to first order in F_0 of any physical measurable such as \hat{P} . This gives a result for the susceptibility,

$$\chi(\omega) = i \text{tr} \int_0^\infty dt' e^{-iH_0 t'} [\hat{Q}, \rho_0] e^{+iH_0 t'} \hat{P} e^{i(\omega+i\eta)t'}. \quad (25)$$

Using the cyclic invariance of the trace, this can be written as

$$\chi(\omega) = i \text{tr} \int_0^\infty dt' [\hat{Q}, \rho_0] \hat{P}(t') e^{i(\omega+i\eta)t'}. \quad (26)$$

where the time dependence of the operator \hat{P} is defined in the usual Heisenberg picture (which is the “interaction” picture relative to the total Hamiltonian $H_0 + H'$)

$$\hat{P}(t) \equiv e^{+iH_0 t} \hat{P} e^{-iH_0 t}. \quad (27)$$

Using again the cyclic invariance of the trace, the answer for χ can be written in a well-known “retarded commutator” form known as the “Kubo formula,”

$$\chi(\omega) = \frac{i}{\hbar} \int_0^\infty dt e^{i\omega t} \langle [\hat{P}(t), \hat{Q}(0)] \rangle \quad (28)$$

$$\chi(t) = \frac{i}{\hbar} \langle [\hat{P}(t), \hat{Q}(0)] \rangle \theta(t). \quad (29)$$

Factors of \hbar , which were previously set to 1, have been restored for this final version. The Heaviside function $\theta(t)$ is 1 when $t > 0$ and 0 otherwise, and the angular brackets denote an equilibrium thermal ensemble average,

$$\langle \hat{D} \rangle \equiv \text{tr} \rho_0 \hat{D} \quad (30)$$

Sometimes it is convenient to have an alternate version where the commutator is eliminated in favor of an integration over imaginary time. This is accomplished by using the operator identity

$$e^{\beta H_0} \hat{Q} e^{-\beta H_0} - \hat{Q} = \int_0^\beta d\lambda \left(e^{\lambda H_0} [H_0, \hat{Q}] e^{-\lambda H_0} \right). \quad (31)$$

which is equivalent to

$$[\hat{Q}, \rho_0] = -i\rho_0 \int_0^\beta d\lambda \dot{\hat{Q}}(-i\lambda) \quad (32)$$

The factor in parentheses in Eq. (31) has been written in shorthand notation as $\dot{\hat{Q}}(-i\lambda)$, where the “dot” denotes a time derivative using the Heisenberg operator equation of motion, and the operator \hat{Q} is given an imaginary time $t = -i\lambda$ using the Heisenberg formula Eq. (27). Applying this identity to Eq. (26), the result is

$$\chi(\omega) = \frac{1}{\hbar} \int_0^\infty dt \int_0^{\beta\hbar} d\lambda e^{i\omega t} \langle \dot{\hat{Q}}(-i\lambda) \hat{P}(t) \rangle. \quad (33)$$

This is an equally well-known version of the “Kubo formula.” One advantage of the elimination of the commutator is that it is easy to take the classical limit ($\hbar \rightarrow 0$) of Eq. (33),

$$\chi_{\text{cl}}(\omega) = \frac{1}{k_B T} \int_0^\infty dt e^{i\omega t} \langle \dot{\hat{Q}}(0) \hat{P}(t) \rangle. \quad (34)$$

All of the preceding formulas are easily generalized to the spatially inhomogeneous case. The perturbing part H' of the Hamiltonian (Eq. (19)) now must be written as

$$H'(t) = - \int d\vec{r} \hat{q}(r) F_0(r) e^{-i(\omega+i\eta)t} \quad (35)$$

where $\hat{q}(r)$ is the operator for the density of the property Q which the field F couples to. The relation of Q to $q(r)$ is the same as the relation of P to $p(r)$ in Eq. (2), except not having the $1/V$ factor. The Kubo formulas for the susceptibility $\chi(r, r'; \omega)$ (Eq. (1)) are now

$$\chi(r, r'; \omega) = \frac{i}{\hbar} \int_0^\infty dt e^{i\omega t} \langle [\hat{p}(r, t), \hat{q}(r', 0)] \rangle \quad (36)$$

$$\chi(r, r'; \omega) = \frac{1}{\hbar} \int_0^\infty dt \int_0^\beta d\lambda e^{i\omega t} \langle \dot{\hat{q}}(r', -i\lambda) \hat{p}(r, t) \rangle. \quad (37)$$

Eqs. (28,33,36,37) are the general forms of the Kubo formula which relate the response functions of a system driven weakly away from equilibrium to the equilibrium fluctuations of corresponding internal densities of the system.

III. ELECTRICAL CONDUCTIVITY

As an example of a Kubo formula, consider the electrical conductivity $\sigma(r, r'; \omega)$ defined as the linear response of the current $j(r)$ to an *ac* electric field $E(r')$. In its fully non-local and tensorial form, this is defined by

$$\langle \hat{j}_\alpha(r, t) \rangle = \int d\vec{r}' \sigma_{\alpha\beta}(r, r'; \omega) E_\beta(r') e^{-i\omega t}. \quad (38)$$

We will drop the vector and tensor subscripts. Most often we are interested in the homogeneous conductivity of either a cubic or a polycrystalline material where the conductivity is a scalar. The current density operator is

$$\hat{j}_{\text{tot}}(r) = \hat{j}(r) + \hat{j}_{\text{dia}}(r) \quad (39)$$

$$\hat{j}(r) = -\frac{e}{2m} \sum_i [p_i \delta(r - r_i) + \delta(r - r_i) p_i]. \quad (40)$$

$$\hat{j}_{\text{dia}}(r) = -\frac{\hat{n}(r) e^2}{mc} \vec{A}(r) \quad (41)$$

$$\hat{n}(r) = \sum_i \delta(r - r_i) \quad (42)$$

When a transverse electromagnetic field is applied, the coupling term in the Hamiltonian is

$$H' = -\frac{1}{c} \int d\vec{r} \hat{j}(r) \cdot \vec{A}(r) e^{-i\omega t}. \quad (43)$$

Only the “paramagnetic” part of the current is kept. The “diamagnetic” part corresponds to the A^2 term in the Hamiltonian which does not affect the linear response. Using the relation $\vec{E} = -(1/c)\partial\vec{A}/\partial t$, the vector potential can be replaced by $cE/i\omega$, and Eq. (43) can be written

$$H' = \int d\vec{r} \int_{-\infty}^t dt \hat{j}(r) \cdot \vec{E}(r, t) = \frac{i}{\omega} \int d\vec{r} \hat{j}(r) \cdot \vec{E}(r) e^{-i\omega t}. \quad (44)$$

The density $\hat{q}(r)$ which couples to E is thus $-i\hat{j}(r)/\omega$, and the conductivity can be written

$$\sigma(r, r'; \omega) = \frac{in(r)e^2}{m\omega} \delta(r - r') + \frac{1}{\hbar\omega} \int_0^\infty dt e^{i\omega t} \langle [\hat{j}(r, t), \hat{j}(r', 0)] \rangle. \quad (45)$$

In the uniform case, this becomes

$$\sigma(\omega) = \frac{ine^2}{m\omega} + \frac{1}{\hbar\omega V} \int_0^\infty dt e^{i\omega t} \langle [\hat{J}(t), \hat{J}(0)] \rangle \quad (46)$$

where $n = N/V$ is the average density of electrons. The first term of Eqs. (45,46) comes from the diamagnetic term Eq. (41) of the current, which flows with no deformation of the state of the system. In the *dc* limit this diverges, but must be cancelled by another divergent term from the second part of the formula. It is convenient to have a formula in which the divergent parts are explicitly cancelled.

In the uniform case this can be accomplished as follows. The uniform current operator \hat{J} is related to the uniform polarization operator $\hat{\Pi}$,

$$\hat{J} = -\frac{e}{m} \sum_i p_i \quad (47)$$

$$\hat{\Pi} = -e \sum_i r_i \quad (48)$$

$$\hat{J} = \dot{\hat{\Pi}} = \frac{i}{\hbar} [H_0, \hat{\Pi}] \quad (49)$$

$$[\hat{\Pi}, \hat{J}] = \frac{iN e^2 \hbar}{m}. \quad (50)$$

Eq. (46) can be replaced by

$$\begin{aligned} \sigma(\omega) &= \frac{ine^2}{m\omega} + \frac{1}{\hbar\omega V} \int_0^\infty dt e^{i(\omega+in)t} \frac{d}{dt} \langle [\hat{\Pi}(t), \hat{J}(0)] \rangle \\ &= \frac{ine^2}{m\omega} - \frac{1}{\hbar\omega V} \langle [\hat{\Pi}(0), \hat{J}(0)] \rangle \\ &\quad - \frac{i}{\hbar V} \int_0^\infty dt e^{i\omega t} \langle [\hat{\Pi}(t), \hat{J}(0)] \rangle \end{aligned} \quad (51)$$

where an integration by parts has been performed. Now the diverging diamagnetic part is cancelled exactly by the equal time commutator (using Eq. (50)) and the conductivity becomes

$$\sigma(\omega) = -\frac{i}{\hbar V} \int_0^\infty dt e^{i\omega t} \langle [\hat{\Pi}(t), \hat{J}(0)] \rangle \quad (52)$$

It is now convenient to remove the commutator, using the identity Eq. (32). The result is

$$\sigma(\omega) = \frac{1}{\hbar V} \int_0^\infty dt \int_0^\beta d\lambda e^{i\omega t} \langle \hat{J}(t - i\lambda) \hat{J}(0) \rangle. \quad (53)$$

There is an alternate route to the results Eq. (52,53) which starts with a different representation for the electric field

$$H' = -\hat{\Pi} \cdot \vec{E} e^{-i\omega t} \quad (54)$$

This form assumes a homogeneous field which can be considered equally well to be longitudinal. Now the quantity Q which couples to the field is $\hat{\Pi}$, and the conductivity follows from Eq. (28),

$$\sigma(\omega) = \frac{i}{\hbar V} \int_0^\infty dt e^{i\omega t} \langle [\hat{J}(t), \hat{\Pi}(0)] \rangle. \quad (55)$$

It is not obvious that Eq. (55) and Eq. (52) are consistent with each other. The commutators $\hat{a} = [\hat{\Pi}(t), \hat{J}(0)]$ and $\hat{b} = [\hat{\Pi}(0), \hat{J}(t)]$ are not the same, but because of the relation Eq. (49), it can be shown that their diagonal matrix elements in the energy representation are the same, which proves consistency. Eq. (55) can be transformed to the version with no commutator,

$$\sigma(\omega) = \frac{1}{\hbar V} \int_0^\infty dt \int_0^\beta d\lambda e^{i\omega t} \langle \hat{J}(-i\lambda) \hat{J}(t) \rangle. \quad (56)$$

Eqs. (45,46,52,53,55,56) are the most important forms of the Kubo formula for the electrical conductivity.

A useful way to analyze Kubo formulas is to expand the thermal averages in a complete set of hypothetical many-body eigenstates $|n\rangle$ of energy E_n of the Hamiltonian H_0 . This is called a spectral representation. If we look only at the real part of $\sigma(\omega)$ for positive values of ω , the result can be written as

$$\text{Re}\sigma_{xx} = \frac{\pi}{V\omega} \sum_{m,n} \frac{e^{-\beta E_n}}{Z} |\langle n|J_x|m\rangle|^2 \delta(\hbar\omega - (E_m - E_n)) \quad (57)$$

This is recognizable as the Fermi ‘‘Golden Rule’’ result that you would get by calculating the power (σE^2) absorbed from the electromagnetic field. This shows that the Kubo formula is really just a fancy way of expressing the Fermi Golden Rule. Both are lowest order time-dependent perturbation theory applied to the perturbation H' using the states of the unperturbed problem H . There are certain advantages to the Kubo formula. One is that sometimes, by heroic computational effort, a direct calculation of the correlation function is possible. Another is that since the exact many-body states are almost never known, one needs powerful many-body perturbation theories to try to evaluate σ accurately, and the Kubo formula provides one possible starting place. However, this route is very difficult. Usually it starts from an unperturbed theory in the form of a free gas. The result of a very tedious calculation is then to acquire a good theory for a not-too-strongly interacting gas, namely Boltzmann transport theory. When the gas becomes too strongly interacting, the Kubo formula is still exact in principle, but the perturbation theory used to evaluate it breaks down. Leading corrections to Boltzmann theory can sometimes be found, but not (by perturbation theory alone) a result that carries over to the strongly-interacting case. Amazingly, it turns out that the Boltzmann theory is quite robust, applying sometimes to strongly interacting situations where simple arguments would suggest that it should fail. Unfortunately there is a common tendency to assume that a Boltzmann theory applies only to a very weakly interacting case, and that a theory based on a Kubo formula (or some other Green’s function starting point) is necessarily better. Very often it turns out that a laborious evaluation of a Kubo or Green’s function expression yields just an approximate solution of the Boltzmann equation; an equally good or perhaps better answer could have been obtained more quickly from the Boltzmann theory directly.

IV. A NON-MECHANICAL CASE: TEMPERATURE GRADIENT

A very interesting case of a non-mechanical perturbation is an applied temperature gradient. The problem is to find the corresponding heat current, or in linear approximation, to find the thermal conductivity, defined by

$$\langle \hat{s}_\alpha(r) \rangle = - \int d\vec{r}' \kappa_{\alpha\beta}(r, r') \frac{\partial T(r')}{\partial r'_\beta} \quad (58)$$

where $\hat{s}(r)$ is the heat current density operator. In principle we could consider a time-varying temperature gradient, but in practise, the time scale on which the temperature varies is so much slower than the microscopic particle relaxation rates that any near-equilibrium thermal perturbation is essentially in the dc limit. Thus the thermal conductivity κ in Eq. (58) is the $\omega \rightarrow 0$ limit of

$\kappa(\omega)$. For a medium with more than one component there is a boundary resistance effect where the temperature drops discontinuously (on a macroscopic scale) across the boundary separating component 1 from component 2 (this is often called the “Kapitsa resistance”) so it is necessary to keep the spatial variables (r, r') . More often, we are interested in a homogeneous medium, and can use the homogeneous version

$$\langle \hat{S} \rangle = -\kappa \nabla T \quad (59)$$

where the vector and tensor subscripts have been dropped, and \hat{S} is the volume average of \hat{s} .

The interesting conceptual problem is that the external driving field, $-\nabla T$, cannot appear in a real Hamiltonian for the system. It is a “non-mechanical” perturbation, so our previous method for deriving a Kubo formula cannot work. This has led to a belief that the Kubo formula for the thermal conductivity has a less rigorous basis than the one for the electrical conductivity. However, in practise a very successful Kubo formula does exist, and a derivation can be given which has no weak point except for the inevitable step of deciding how to think about a situation where thermal equilibrium is defined locally rather than globally. Since temperature is an equilibrium concept, defined by reference to a heat bath and giving rise to Boltzmann-weighted thermal averages, if a spatially-varying temperature can be discussed, it must be attributed similar statistical properties. This leads (inevitably, I think) to the local-equilibrium density matrix

$$\hat{\rho}_{\text{LE}} = \frac{1}{Z} \exp \left[- \int d\vec{r} \beta(r) \hat{h}(r) \right] \quad (60)$$

Here $\hat{h}(r)$ is a Hamiltonian density operator which when integrated over space gives the Hamiltonian H_0 ,

$$H_0 = \int d\vec{r} \hat{h}(r). \quad (61)$$

The temperature is a constant, $T = 1/\beta k_B$, plus a small variation $\delta T(r)$, so $\beta(r)$ can be expanded,

$$\beta(r) = \beta \left[1 - \frac{\delta T(r)}{T} \right]. \quad (62)$$

Using Eqs. (62,61) in Eq. (60) gives

$$\hat{\rho}_{\text{LE}} = \frac{1}{Z} e^{-\beta(H_0 + H_{\text{eff}'})} \quad (63)$$

which defines an “effective thermal perturbation”

$$H_{\text{eff}'} = -\frac{1}{T} \int d\vec{r} \delta T(r) \hat{h}(r) \quad (64)$$

which appears in the density matrix as if it were an actual external perturbation. It is convenient to rewrite this replacing the Hamiltonian density by the heat current operator. The relation between these operators is the condition of local energy conservation which must hold over macroscopic distance scales,

$$\frac{\partial \hat{h}(r)}{\partial t} = -\vec{\nabla} \cdot \hat{s}(r) \quad (65)$$

$$\hat{h}(r) = - \int dt \vec{\nabla} \cdot \hat{s}(r). \quad (66)$$

Using Eq. (66) in Eq. (64), and integrating by parts, the effective perturbation is

$$H_{\text{eff}'} = -\frac{1}{T} \int d\vec{r} \int dt \vec{\nabla} T(r) \cdot \hat{s}(r) \quad (67)$$

$$H_{\text{eff}'} = -\frac{V}{T} \int_{-\infty}^0 dt \vec{\nabla} T \cdot \hat{S}(t). \quad (68)$$

The second form assumes a homogeneous temperature gradient. The time argument and limits of integration are shown explicitly. The time integration ends at $t = 0$ which is the time when the density matrix is needed. This has precisely the same form as the perturbing Hamiltonian Eq. (44) in the electrical case, with the \vec{E} field replaced by $-\vec{\nabla} T$, and the electrical current density \hat{j} replaced by \hat{s}/T .

The Kubo formula follows once we make a perturbative expansion of the density matrix to first order in $H_{\text{eff}'}$. This can be done using another operator identity. Define a quantity

$$U(\lambda) \equiv e^{\lambda H_0} e^{-\lambda(H_0 + H')} \quad (69)$$

$$\frac{dU}{d\lambda} = - \left(e^{\lambda H_0} H' e^{-\lambda H_0} \right) U(\lambda). \quad (70)$$

Integrate both sides over λ from 0 to β to get

$$U(\beta) = 1 - \int_0^\beta d\lambda H'(-i\lambda) U(\lambda). \quad (71)$$

Finally, solve iteratively for $U(\beta)$ to first order in H' ,

$$\rho_{\text{LE}} \approx \rho_0 - \rho_0 \int_0^\beta d\lambda H'(-i\lambda). \quad (72)$$

Now we can calculate the thermal conductivity which is the heat current density $\langle\langle \hat{S} \rangle\rangle_{\text{LE}}$ in the local equilibrium situation divided by the negative temperature gradient,

$$\kappa = \frac{V}{T} \text{tr} \int_0^{\beta\hbar} d\lambda \int_{-\infty}^0 dt \hat{S}(t - i\lambda) \hat{S}(0). \quad (73)$$

To put this in a more conventional form, the invariance under time translations permits us to subtract t from all the time arguments. Then as a new variable of integration, use $-t$. The result is

$$\kappa = \frac{V}{T} \int_0^{\beta\hbar} d\lambda \int_0^\infty dt \langle \hat{S}(-i\lambda) \hat{S}(t) \rangle. \quad (74)$$

This version of the Kubo formula is completely parallel to Eq. (56) in the electrical case.

V. FLUCTUATION-DISSIPATION THEOREM

The ‘‘fluctuation-dissipation theorem’’ is a result which relates the linear response coefficients χ (which describe, among other things, dissipative effects and the irreversible approach of a system to equilibrium) to simpler correlation functions describing fluctuations which occur in the system in equilibrium. As a prototype correlation function $C(t)$, we write

$$C(t) = \langle \hat{P}(t)\hat{Q}(0) \rangle. \quad (75)$$

This must be related somehow to the response coefficient Eq. (29)

$$\chi(t) = \frac{i}{\hbar} \langle [\hat{P}(t), \hat{Q}(0)] \rangle \theta(t). \quad (76)$$

The relation is discovered by expressing the Fourier transform in a basis of exact eigenstates $|n\rangle$ with energy E_n of the system Hamiltonian H_0 .

$$\begin{aligned} C(\omega) &= \int_{-\infty}^{\infty} dt e^{i\omega t} C(t) \\ &= \frac{2\pi}{Z} \sum_{i,f} e^{-\beta E_i} \langle i|\hat{P}|f\rangle \langle f|\hat{Q}|i\rangle \delta(\omega + E_i - E_f) \end{aligned} \quad (77)$$

where Z is the partition function. Doing the same for $\chi(\omega)$ gives

$$\begin{aligned} \chi(\omega) &= \int_0^{\infty} e^{i(\omega+i\eta)t} \chi(t) \\ &= - \sum_{i,f} \frac{e^{-\beta E_i} - e^{-\beta E_f}}{Z} \left[\frac{\langle i|\hat{P}|f\rangle \langle f|\hat{Q}|i\rangle}{\omega + i\eta + E_i - E_f} \right] \end{aligned} \quad (78)$$

To make Eq. (79) look more like Eq. (78), we convert the energy denominators into delta functions by taking the imaginary part. This only works if the numerators are real. When the operators \hat{P} and \hat{Q} are proportional to each other, as is most often the case, then the numerators are $|\langle i|\hat{Q}|f\rangle|^2$ and therefore real. Let us assume that these numerators are real. Thus we get

$$\begin{aligned} \text{Im}\chi(\omega) &= \frac{\pi}{Z} \sum_{i,f} (e^{-\beta E_i} - e^{-\beta E_f}) \langle i|\hat{P}|f\rangle \langle f|\hat{Q}|i\rangle \delta(\omega + E_i - E_f) \\ &= \frac{\pi(1 - e^{-\beta\hbar\omega})}{Z} \sum_{i,f} e^{-\beta E_i} \langle i|\hat{P}|f\rangle \langle f|\hat{Q}|i\rangle \delta(\omega + E_i - E_f) \end{aligned} \quad (79)$$

Comparing Eqs. (78,80), we have the ‘‘fluctuation-dissipation theorem’’,

$$\text{Im}\chi(\omega) = \frac{1}{2\hbar} (1 - e^{-\beta\hbar\omega}) C(\omega). \quad (80)$$

This is valid for any correlation function and corresponding susceptibility where the operators \hat{P} and \hat{Q} are proportional. The next two sections contain applications of this theorem.

VI. DENSITY RESPONSE; DIELECTRIC SCREENING; NEUTRON SCATTERING

Probably the most important application of linear response theory in condensed matter physics is the response to an external field which couples to the electron density. The electron density operator $\hat{\rho}(r)$ measures the electron density at point r :

$$\hat{\rho}(r) = \sum_i \delta(r - r_i). \quad (81)$$

An external scalar potential $V_{\text{ext}}(r, t)$ will couple linearly to electron density:

$$H'(t) = \int d\vec{r} \hat{\rho}(r) V_{\text{ext}}(r, t). \quad (82)$$

The potential V_{ext} could be for example $e\vec{E} \cdot \vec{r}$ from external capacitor plates, or $-Ze^2/|R(t) - r|$ from a point charge Ze located at $R(t)$. In linear approximation (*i.e.*, accurate when $Z \ll 1$) the system produces an electron density disturbance or screening charge $\delta\rho_{\text{ind}}$ in response,

$$\langle \delta\rho_{\text{ind}}(r, t) \rangle = \int d\vec{r}' \int_{-\infty}^t dt' \chi(r, r'; t - t') V_{\text{ext}}(r', t') \quad (83)$$

which defines the “density” susceptibility χ . From Eq. (29),

$$\chi(r, r', t - t') = -\frac{i}{\hbar} \langle [\hat{\rho}(r, t), \hat{\rho}(r', t')] \rangle \theta(t - t') \quad (84)$$

where the minus sign occurs because the operator playing the role of \hat{Q} in Eq. (19) is $-\hat{\rho}$ in Eq. (82), while the operator \hat{P} is $\hat{\rho}$. From the electron density susceptibility, the dielectric function can be immediately calculated.

An important related correlation function is the density correlation function $P(r, r'; t)$ defined as

$$P(r, r'; t) = \langle \hat{\rho}(r, t) \hat{\rho}(r', 0) \rangle \quad (85)$$

which determines the probability of finding an electron at point (r, t) if there was one at point $(r', 0)$. The time Fourier transforms of P and χ are related by the fluctuation-dissipation theorem,

$$P(r, r'; \omega) = -\frac{2\hbar}{1 - e^{-\beta\hbar\omega}} \text{Im}\chi(r, r'; \omega) \quad (86)$$

An application of these formulas is in scattering theory, especially neutron scattering. A neutron couples to nuclear density, so we should now interpret the operator $\hat{\rho}$ in Eq. (81) *ff* as referring to nuclear density. In Born approximation, which is very accurate for neutron interactions with matter, the cross section for neutron scattering with energy loss ω and momentum loss \vec{q} is the frequency and wavevector Fourier transform of $P(r, r'; t - t')$, while the corresponding Fourier transform of χ is a form of vibrational Green’s function. If the frequency ω is positive, this corresponds to a neutron losing energy to the lattice, and the cross section can be written using Eq. (86)

$$\frac{d^2\sigma}{d\Omega d\omega} \propto P(q, \omega) = -2\hbar[n(\omega) + 1] \text{Im}\chi(q, \omega) \quad (87)$$

where $n(\omega)$ is the Bose-Einstein occupation number $1/(\exp(\beta\hbar\omega) - 1)$. Negative values of the frequency correspond to scattering with an energy gain. Again using Eq. (86), and the fact that $\text{Im}\chi(\omega)$ is odd in ω , this can be written as

$$\frac{d^2\sigma}{d\Omega d\omega} \propto P(q, -\omega) = -2\hbar n(|\omega|) \text{Im}\chi(q, |\omega|) \quad (88)$$

Thus we obtain the usual Einstein population factors for absorption of a vibrational quantum ($n(\omega)$) and for stimulated emission ($n + 1$).

VII. ELECTRONIC FRICTION ON A PARTICLE MOVING IN A METAL

Consider a particle of mass M located at time t and point $R(t)$ in a metal. In a classical picture, such as is used for example in a “molecular dynamics” simulation, this particle obeys the Newtonian equation

$$M\ddot{R} = -\nabla_R U(R; R_1, \dots, R_N) \quad (89)$$

where R_i is the coordinate of one of the N “ordinary” atoms of the system, and R is the “special” particle under consideration. For example, the special particle might be a proton in a Pd host, and the other atoms are the palladium atoms. In such an equation, the electronic degrees of freedom are all hidden in the adiabatic total energy U , which is the total energy of the system of proton, palladium nuclei, and electrons, calculated with the nuclei all stationary.

In a metal, the Born-Oppenheimer (adiabatic) approximation is not guaranteed to be sufficiently accurate, and in particular, it may happen that by inelastic collisions between the “particle” and the electrons there is a significant extra frictional damping not already accounted for in the adiabatic Eq. (89). In such a case, the Langevin equation is available to simulate this additional friction,

$$M\ddot{R} = -\nabla_R U(R; R_1, \dots, R_N) - M\eta\dot{R} + F_{\text{st}}(t) \quad (90)$$

where η is a friction coefficient, and $F_{\text{st}}(t)$ is a “stochastic force”, that is, a random force with time average $\langle F_{\text{st}}(t) \rangle = 0$. This stochastic force is needed to keep the temperature of the system from irreversibly decreasing to zero under the influence of the friction. The mean square magnitude of $F_{\text{st}}(t)$ is fixed by

$$\langle F_{\text{st}}(t)F_{\text{st}}(t') \rangle = 2M\eta k_B T \delta(t - t') \quad (91)$$

An interesting question is how would one make the correct realistic choice of the friction coefficient η ? We can use the techniques of linear response theory to answer this question, and in the process, obtain a microscopic derivation of Eqs. (90,91). The correct treatment of friction turns out to replace these results by more complicated ones where the friction is retarded in time. The interaction between the proton and an electron, $-e^2/|R - r|$, will be denoted $V_{\text{pe}}(R - r)$. The force on the proton due to all electrons in the system is

$$F_{\text{pe,tot}}(t) = - \int d\vec{r} \nabla_R V_{\text{pe}}(R - r) \quad (92)$$

$$\times \left(\langle \hat{\rho}(r, t) \rangle_0 + \langle \delta\rho_{\text{ind,AD}}(r, t) \rangle + \langle \delta\rho_{\text{ind,NON-AD}}(r, t) \rangle + [\rho(r, t) - \langle \rho(r, t) \rangle] \right).$$

The first two parts of this equation are the force which the proton feels due to the electronic charge of the crystal undisturbed by the proton’s presence, and the correction due to the proton’s presence, calculated in adiabatic approximation. Since the ions of the lattice are heavy compared to the proton, their speeds of thermal motion are slow, and we assume that the adiabatic approximation is sufficiently good for the first part. These first two parts are then already included in the Newtonian Eq. (89). The third term represents the correction from the time-dependence of the proton motion. Since the proton has a small mass, its thermal velocity is sufficiently large that the Born-Oppenheimer approximation needs to be corrected. Since the correction is expected to be small, we will calculate it in linear approximation. The last term (the one in square brackets) is quite interesting. The angular brackets in the first three terms indicate a thermal ensemble average. This should give correctly the time average of the electron density and the corresponding force on the proton. The actual density

and force will fluctuate around this time average in a way which we might imagine trying to calculate by forward integration of the time-dependent Schrödinger equation for the whole system, assuming as a boundary condition some choice of many body wavefunction at some time in the past. This calculation would be daunting, and the details of the precise time-evolution of fluctuations should not matter very much anyway for a proper understanding of the proton's motion. Therefore it may be sufficient to model correctly the statistical behavior of this fluctuating electron density rather than its actual behavior. In the Langevin Eq. (90), the friction models the third term of Eq. (93) and the stochastic force models the fourth.

From the previous section, we know how to represent the induced electron density which arises from the presence of the proton, at least in linear approximation,

$$\langle \delta \rho_{\text{ind, TOT}}(r, t) \rangle = \int d\vec{r}' \int_{-\infty}^t dt' \chi(r, r'; t - t') V_{\text{pe}}(R(t') - r'). \quad (93)$$

The total induced density depends on the trajectory $R(t')$ of the proton at all previous times. In first approximation, the electronic susceptibility decays exponentially as $\exp(-|t - t'|/\tau)$ with some decay time τ which is similar to the time τ in the conductivity formula $ne^2\tau/m$. The reciprocal \hbar/τ is a lifetime-broadening which is typically at least as large as $k_B T$, i.e. 25meV at 300K. This corresponds to a sufficiently short time that we may perhaps replace $R(t')$ in Eq. (93) by $R(t)$, that is, we may make the adiabatic approximation. The correction to the adiabatic approximation $\langle \delta \rho_{\text{ind, NON-AD}} \rangle$, is then found by replacing $V_{\text{pe}}(R(t') - r')$ in Eq. (93) by $\Delta V \equiv V_{\text{pe}}(R(t') - r') - V_{\text{pe}}(R(t) - r')$. It is now convenient to introduce the following derivatives,

$$\frac{d}{dt} \Delta V = \vec{\nabla}_R V_{\text{pe}}(R(t') - r') \cdot \dot{R}(t') \quad (94)$$

$$\chi(r, r'; t - t') \equiv \frac{d}{dt'} \zeta(r, r'; t - t') \quad (95)$$

where the last equation defines a new response function ζ whose time derivative is χ . Using these derivative expressions, we can write the non-adiabatic density response as

$$\begin{aligned} \langle \delta \rho_{\text{ind, NON-AD}}(r, t) \rangle &= \int d\vec{r}' \int_{-\infty}^t dt' \frac{d\zeta(r, r'; t - t')}{dt'} \Delta V(t') \\ &= - \int d\vec{r}' \int_{-\infty}^t dt' \zeta(r, r'; t - t') \nabla_R V_{\text{pe}}(R(t') - r') \dot{R}(t'). \end{aligned} \quad (96)$$

where the time integration has been rearranged by integration by parts. Going back to Eq. (93), we now have a formula for the non-adiabatic force on the proton,

$$F_{\text{pe, NON-AD}} = -M \int_{-\infty}^t dt' \eta(R(t), R(t'); t - t') \dot{R}(t') \quad (97)$$

$$M\eta(R, R'; t - t') = - \int d\vec{r} d\vec{r}' \nabla_R V_{\text{pe}}(R - r) [\zeta(r, r'; t - t')] \nabla_R V_{\text{pe}}(R' - r') \quad (98)$$

Clearly this is a frictional force, very similar to the phenomenological force $-M\eta\dot{R}$ appearing in the Langevin Eq. (90), except retarded in time. Also, there is an implicit trajectory-dependence in the factors $\nabla_R V_{\text{pe}}(R(t) - r)$ which determine the end-points to which the “friction propagator” $\zeta(r, r'; t - t')$ gets integrated.

When would it be valid to use the instantaneous friction of the phenomenological Langevin equation? The friction propagator ζ is related by a time derivative (Eq. (95)) to the density susceptibility, and therefore has the same decay time τ . During this decay time, the proton's position R and velocity $v = \dot{R}$ have changed by $\Delta R = v\tau$ and $\Delta v = F\tau/M$ respectively, where F represents the total force felt by the proton. This force is the same in magnitude as the typical force on a valence electron in a solid, that is, a few eV per Å. A good approximate formula is $F \approx \epsilon_F/a$ where ϵ_F is the Fermi energy and a is the lattice spacing. The "implicit" trajectory dependence through $\nabla_R V_{pe}$ disappears provided $\Delta R/a \ll 1$; the velocity $\dot{R}(t')$ in Eq. (97) can be replaced by the instantaneous velocity $\dot{R}(t)$ provided $\Delta v/v \approx \epsilon_F\tau/Mva \ll 1$. The thermal momentum Mv of the proton is $2\pi\hbar/\lambda$ where λ is the thermal DeBroglie wavelength. A factor \hbar^2/Ma^2 can be replaced by $(m/M)\epsilon_F$ where (m/M) is the electron to proton mass ratio. The decay rate \hbar/τ is of order $k_B T$. Thus the criteria are

$$\frac{\Delta R}{a} \ll 1 \quad \text{or} \quad \frac{m}{M} \cdot \frac{2\pi a}{\lambda} \ll \frac{k_B T}{\epsilon_F} \quad (99)$$

$$\frac{\Delta v}{v} \ll 1 \quad \text{or} \quad \frac{\lambda}{2\pi a} \ll \frac{k_B T}{\epsilon_F} \quad (100)$$

At 1000K the proton thermal wavelength is of order 0.5\AA . The first criterion is well-satisfied, but the second is only marginal. However, if we are interested in superthermal protons (e.g., protons slowing down from higher than thermal velocities, or protons with accidentally high energies attempting to climb over saddle points in a diffusion process) then the appropriate value of λ is even smaller, and both criteria may be satisfied. Then we recover the Langevin equation with the friction coefficient equal to

$$\eta = \int_{-\infty}^t dt' \eta(R, R; t - t'). \quad (101)$$

Now it is time to examine the last term of Eq. (93). The time-correlation of this force with itself is

$$\langle F_{st}(R, t) F_{st}(R', t') \rangle = \int d\vec{r} \int d\vec{r}' \nabla_R V_{pe}(R - r) [\langle \delta\hat{\rho}(r, t) \delta\hat{\rho}(r', t') \rangle] \nabla_{R'} V_{pe}(R' - r'). \quad (102)$$

The factor in square brackets in this equation can be written as the time transform of a frequency dependent correlation function,

$$\begin{aligned} [\langle \delta\hat{\rho}(r, t) \delta\hat{\rho}(r', t') \rangle] &= \int_{-\infty}^{\infty} \frac{d\omega}{2\pi} e^{-i\omega(t-t')} P(r, r'; \omega) \\ &= \int_{-\infty}^{\infty} \frac{d\omega}{2\pi} e^{-i\omega(t-t')} \left[-\frac{2\hbar \text{Im}\chi(r, r'; \omega)}{1 - e^{-\beta\hbar\omega}} \right] \end{aligned} \quad (103)$$

where the fluctuation-dissipation theorem Eq. (86) has been used. Similarly, the factor in square brackets in the friction coefficient Eq. (98) can be written as the time transform of the frequency dependent friction propagator

$$[\zeta(r, r'; t - t')] = \int_{-\infty}^{\infty} \frac{d\omega}{2\pi} e^{-i\omega(t-t')} \left[-\frac{\chi(r, r'; \omega)}{i\omega} \right] \quad (104)$$

Eqs. (98 and 102-104) contain the relation between the time correlation of the stochastic force and the retarded friction coefficient, generalizing the Eq. (91) of the phenomenological Langevin theory.

Under the conditions where Eq. (101) applies. When this works, we can replace Eqs. (98,101, and 104) by

$$M\eta = - \int d\vec{r} \int d\vec{r}' \nabla_R V_{pe}(R-r) \lim_{\omega \rightarrow 0} \left[\frac{\text{Im}\chi(r, r'; \omega)}{\omega} \right] \nabla_R V_{pe}(R-r'). \quad (105)$$

At the same level of approximation, the correlation function in Eq. (104) decays rapidly to zero as $(1/2\tau) \exp(-|t-t'|/\tau)$. For small τ , this becomes $\delta(t-t')$. To determine the weight W of the delta function, we do the time integral

$$W \equiv \int_{-\infty}^{\infty} dt \langle F_{st}(R, t) F_{st}(R, t') \rangle \quad (106)$$

where the time-dependence of R, R' are neglected. Using Eqs. (102,104) we obtain exactly $2M\eta k_B T$, the result of Eq. (91). This seems to be the microscopic justification of the Langevin equation.