

frequencies

$$\chi(z) \sim -\frac{1}{z} \sum_{n=0}^{\infty} \int_{-\infty}^{\infty} \frac{d\omega}{\pi} \chi''(\omega) \left(\frac{\omega}{z}\right)^n \quad (23)$$

and which is valid for large enough z provided

$$\int_{-\infty}^{\infty} \frac{d\omega}{\pi} \chi''(\omega) \omega^n \quad (24)$$

converges. Comparing coefficients for large z , we have for our phenomenological models

$$\chi(z) \sim -\frac{1}{mz^2} = -\frac{1}{z^2} \int_{-\infty}^{\infty} \frac{d\omega}{\pi} \chi''(\omega) \omega. \quad (25)$$

This is a well-known sum-rule, which is generally valid, i.e.,

$$\int_{-\infty}^{\infty} \frac{d\omega}{\pi} \chi''(\omega) \omega = \frac{1}{m}. \quad (26)$$

For our example, we have

$$\int_{-\infty}^{\infty} \frac{d\omega}{\pi} \frac{\omega^2 \gamma}{[(\omega^2 - \omega_0^2)^2 + (\gamma\omega)^2]} = \frac{1}{m}.$$

If we take our phenomenological expressions seriously, however, we see that they give a divergent result for

$$\int_{-\infty}^{\infty} \frac{d\omega}{\pi} \chi''(\omega) \omega^3.$$

We may begin to understand why this is a failing of the phenomenological models by recalling the derivation of the radiation damping expression. In that derivation one assumes that $\omega e^2/mc^3 \ll 1$. For times short (frequencies high) compared to the time it takes a light signal to cross a classical electron, one must consider the actual radiation processes more carefully. When one does, the damping no longer increases like the cube of the frequency. In fact, for any system, the relation between the internal force and the displacement must vanish at high frequencies. It takes time for the medium to respond to the fact we have forced the oscillator. Not only does the restoring force vanish at high frequencies; it vanishes faster than any power of the frequency so that in a microscopic theory, and in a physical measurement of $\chi''(\omega)$, we have a free oscillator as $\omega \rightarrow \infty$;

$$\int_{-\infty}^{\infty} \frac{d\omega}{\pi} \chi''(\omega) \omega^n$$

is finite for all n . ($\chi''(\omega) \rightarrow \pi\delta(\omega^2 - \omega_0^2)\omega/|\omega|$ plus small corrections.)

We can give a quick proof of these claims about the existence of all moments² by invoking a famous and useful theorem, the Nyquist theorem (or fluctuation-dissipation theorem) which we shall subsequently prove. According to this theorem the dissipation that results when an external field is applied to the system is simply related to the fluctuations in thermodynamic equilibrium. Thus our discussion of $\chi''(\omega)$ or $\chi(\omega)$ is literally as indicated in the first paragraph, a calculation of the behavior of the oscillator when no external forces are applied.

Specifically, the Nyquist theorem says that

$$\begin{aligned} \langle x(t) x(t') \rangle_{\text{eq.}} &= \langle x(t) \rangle_{\text{eq.}} \langle x(t') \rangle_{\text{eq.}} = (\langle x(t) x(t') \rangle_{\text{eq.}}) \\ &= \int \frac{d\omega}{2\pi} e^{-i\omega(t-t')} 2\epsilon(\omega) \chi''(\omega) / i\omega \end{aligned} \quad (27)$$

where $\epsilon(\omega)$ is the mean energy of an oscillator with natural frequency ω at temperature $kT = \beta^{-1}$, that is,

$$\epsilon(\omega) \equiv \hbar\omega \left[\frac{1}{2} + \frac{1}{e^{\beta\hbar\omega} - 1} \right] \rightarrow \frac{1}{\beta} \quad \text{class.} \quad (28)$$

Thus the statement we previously indicated was a general sum rule

$$\int_{-\infty}^{\infty} \frac{d\omega}{\pi} \chi''(\omega) \omega = \frac{1}{m} \quad (29)$$

is at least classically, just the statement

$$\frac{1}{2} m \langle \dot{x}^2(t) \rangle = \int \frac{d\omega}{2\pi} \frac{m}{\beta} \omega \chi''(\omega) = \frac{1}{2} kT \quad (30)$$

i.e., the statement that the mean kinetic energy of the oscillator is $\frac{1}{2} kT$.

But by exactly the same kind of argument, we have

$$\langle \dot{x}^2(t) \rangle = \int \frac{d\omega}{\pi} \frac{\omega^3}{\beta} \chi''(\omega) \quad (31)$$

$$\left\langle \left(\frac{d^n x(t)}{dt^n} \right)^2 \right\rangle = \int \frac{d\omega}{\pi} \frac{\omega^{2n-1}}{\beta} \chi''(\omega) \quad (32)$$

and the thermodynamic average of the squares of the higher derivatives of the position are all finite. One can, for example, calculate $\langle \dot{x}^2(t) \rangle$ directly for an oscillator interacting with particles by a potential $\sum_{\alpha} v(x(t) - x_{\alpha}(t))$, deducing

$$\begin{aligned} \langle \dot{x}^2(t) \rangle &\equiv \frac{kT}{m} \omega_{\infty}^2 \equiv \frac{kT}{m} \langle \omega_{n\infty}^2 \rangle \\ \omega_{\infty}^2 &= \frac{n}{3m} \int d^3r g(r) \nabla^2 v(r) + \omega_0^2 \end{aligned} \quad (33)$$

where $g(\nu)$ is the equilibrium correlation function between the medium and oscillator.

It is possible to incorporate this "sum rule" by modifying our simplest phenomenological model. In particular we may introduce a description like the ones employed by Drude and Maxwell at the turn of the century. We suppose that the induced internal force satisfies the phenomenological law

$$\frac{1}{(\omega_0^2 - \omega_0^2)} \frac{\partial \delta \langle F^{\text{int}} \rangle_{n.e.}}{\partial t} + \frac{\delta \langle F^{\text{int}} \rangle_{n.e.}}{\gamma} = - \frac{m \delta \langle \dot{x} \rangle_{n.e.}}{\partial t} \quad (34)$$

which interpolates between the high frequency reactive behavior characterized by (33), and the low frequency phenomenological damping when $\omega < \tau \equiv (\omega_\infty^2 - \omega_0^2)/\gamma$, or

$$\delta \langle F^{\text{int}} \rangle_{n.e.} = \frac{m i \omega \tau}{1 - i \omega \tau} (\omega_0^2 - \omega_0^2) \delta \langle x \rangle_{n.e.} \quad (35)$$

This phenomenological law, which of course is still not really adequate since it predicts

$$\int \omega^5 \chi''(\omega) \frac{d\omega}{\pi} = \infty,$$

gives a familiar kind³ of expression for $\chi(z)$, namely, for $\text{Im } z > 0$,

$$\chi^{-1}(z) = -m \left[z^2 - \omega_0^2 + \frac{(\omega_\infty^2 - \omega_0^2) \tau z i}{1 - iz \tau} \right]; \quad \gamma = (\omega_\infty^2 - \omega_0^2) \tau. \quad (36)$$

Instead of introducing successively more satisfactory phenomenological descriptions which will always be somewhat ad hoc, let us write the almost tautological equation (which we shall also discuss more formally at a later stage)

$$\chi^{-1}(z) \equiv -m[z^2 - \omega_0^2 + iz\gamma(z)]. \quad (37)$$

In this equation we have replaced the unknown response function $\chi(z)$ by an equally unknown function $\gamma(z)$

$$\gamma(z) = \int \frac{d\omega'}{\pi i} \frac{\gamma'(\omega')}{\omega' - z} \rightarrow \gamma'(\omega) + i\gamma''(\omega) \quad \text{as } z = \omega + i\epsilon \rightarrow \omega \quad (38)$$

$$\gamma''(\omega) = -P \int \frac{d\omega'}{\pi} \frac{\gamma'(\omega')}{\omega' - \omega} \quad (39)$$

in which $\gamma(z)$ is associated with the phenomenological law. For an oscillator of the type considered, symmetry properties require that $\gamma'(\omega)$ is real, even and positive so the oscillator is described by

$$\chi^{-1}(z) = -m \left[z^2 - \omega_0^2 + z^2 \int \frac{d\omega'}{\pi} \frac{\gamma'(\omega')}{\omega'^2 - z^2} \right] \quad (40)$$

$$\text{or} \quad \gamma''(\omega) = \frac{1}{m} \frac{\omega \gamma'(\omega)}{(\omega^2 - \omega_0^2 - \omega \gamma'(\omega))^2 + (\omega \gamma''(\omega))^2} \quad (41)$$

These expressions in terms of γ rigorously describe the properties of an oscillator coupled to its surroundings in any time-reversal invariant system. The great variety of possible behaviors manifests itself in the diverse possibilities for $\gamma(z)$. Depending on the coupling there may be one or many "renormalized" natural frequencies, $\bar{\omega}$, of the oscillator, that is, solutions to the equation

$$\bar{\omega}^2 - \omega_0^2 - \bar{\omega} \gamma'(\bar{\omega}) = 0. \quad (42)$$

These solutions will be of interest if the quantity $\omega \gamma'(\omega)$ is small and slowly varying near $\bar{\omega}$ since, in the neighborhood of $\bar{\omega}$, they correspond to resonances.⁴ They will be true normal modes of the oscillator if $\gamma'(\bar{\omega}) = 0$.

In the neighborhood of a relatively well defined mode or *resonant frequency*, $\bar{\omega}$, we may write

$$\begin{aligned} \gamma'(\omega) &\cong \frac{1}{m} \frac{Z(\bar{\omega}) \bar{\omega} \gamma'(\bar{\omega})}{(\omega^2 - \bar{\omega}^2)^2 + (\bar{\omega} \gamma'(\bar{\omega}))^2} \\ \omega \gamma''(\omega) &\cong \frac{1}{2m} \frac{Z(\bar{\omega}) \frac{1}{2} \bar{\gamma}'(\bar{\omega})}{(\omega - \bar{\omega})^2 + (\frac{1}{2} \bar{\gamma}'(\bar{\omega}))^2} \end{aligned} \quad (43)$$

where we have introduced

$$\bar{\gamma}'(\bar{\omega}) = Z(\bar{\omega}) \gamma'(\bar{\omega}) \quad (44)$$

and

$$Z^{-1}(\bar{\omega}) \cong 1 - \frac{\partial}{\partial \bar{\omega}^2} \bar{\omega} \gamma'(\bar{\omega}). \quad (45)$$

The quantity $\frac{1}{2} \bar{\gamma}'(\bar{\omega})$ is the half-width at half-height of the resonance and describes the *rate* at which the oscillator amplitude decays. The energy of the oscillator, quadratic in the amplitude, decays at the rate $\bar{\gamma}'(\bar{\omega})$ in the neighborhood of the resonance. The quantity, $Z(\bar{\omega})$, the renormalization constant, represents the *strength* or fraction of the oscillator motion which participates in the approximate normal mode, $\bar{\omega}$, of the coupled system; or more precisely, (when $\bar{\gamma}'$ is small but not zero) in the many normal modes centered about $\bar{\omega}$. Because γ' is positive, $d\bar{\omega} \gamma'(\bar{\omega})/d\bar{\omega}^2 < 0$, so that the fraction, $Z(\bar{\omega})$, in any normal mode is less than unity. Describing each resonance, therefore, there are three parameters: resonant frequency, lifetime, and strength. For the uncoupled oscillator, $\bar{\omega} = \pm \omega_0$, $\bar{\gamma}'(\bar{\omega}) = 0$, and $Z(\bar{\omega}) = 1$. If the oscillator were coupled to a single other oscillator with frequency $\bar{\omega}_0$ we would have⁵

$$\gamma'(\omega) = \pi \lambda \delta(\bar{\omega}_0^2 - \omega^2).$$

There would then be two normal modes; two roots $\bar{\omega}_1^2$ and $\bar{\omega}_2^2$. Each would have infinite lifetime ($\bar{\gamma}'(\bar{\omega}_i) = 0$) and $Z(\bar{\omega}_1) + Z(\bar{\omega}_2) = 1$. See Fig. 8.

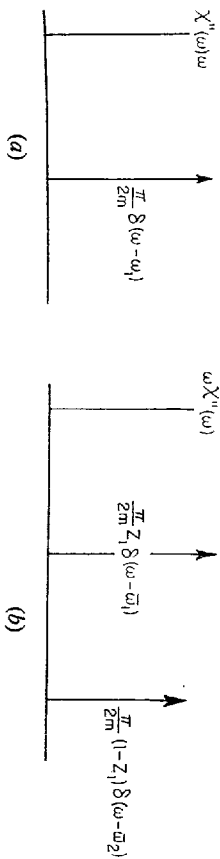


Fig. 8(a). The absorption $\omega\chi''(\omega)$ for an uncoupled oscillator. (b) The absorption $\omega\chi''(\omega)$ for an oscillator coupled to another oscillator, the normal frequencies of the pair being ω_1 and ω_2 . The quantity Z_1 represents the fraction of the first oscillator displacement in the first (normalized) normal mode.

An example of the way a coupled oscillator exhibits both normal modes is provided in a recent experiment by one of the participants in these lectures, Dr. Wright. In an experiment in which Raman scattering by a longitudinal optical phonon was observed⁶ he found that by altering the carrier concentration in GaAs he could alter the plasma frequency, ω_p , and the coupling of the plasma mode to the longitudinal optical mode, ω_1 . The resultant $\chi(\omega)$ is schematically given by

$$\chi^{-1}(z) \propto \left[z^2 - \omega_1^2 + \frac{\alpha\omega_p^2}{\omega_p^2 - z^2} \right]. \quad (46)$$

The variation of the two resultant peaks with ω_p^2 is shown in Fig. 9.

The weak coupling to infinitely many modes, by contrast, will frequently lead to a reduction in $Z(\bar{\omega})$ from unity at a single resonance, without the appearance of any additional resonance. These properties are depicted in Fig. 10.

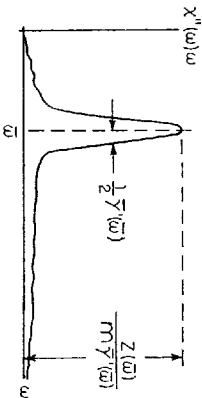


Fig. 10. The absorption in an oscillator coupled to many degrees of freedom, as in Fig. 7. The significance of the renormalized frequency $\bar{\omega}$, the half width $\frac{1}{2}\gamma'(\bar{\omega})$, and the strength $Z(\bar{\omega})$, are shown.

The oscillator strength, originally lodged in the discrete mode is now shared among the infinitely many modes of the coupled system. Part of it, a fraction defined by Z , is shared in a fashion described by a Lorentzian, over nearby modes. The remainder is divided in a model dependent fashion.

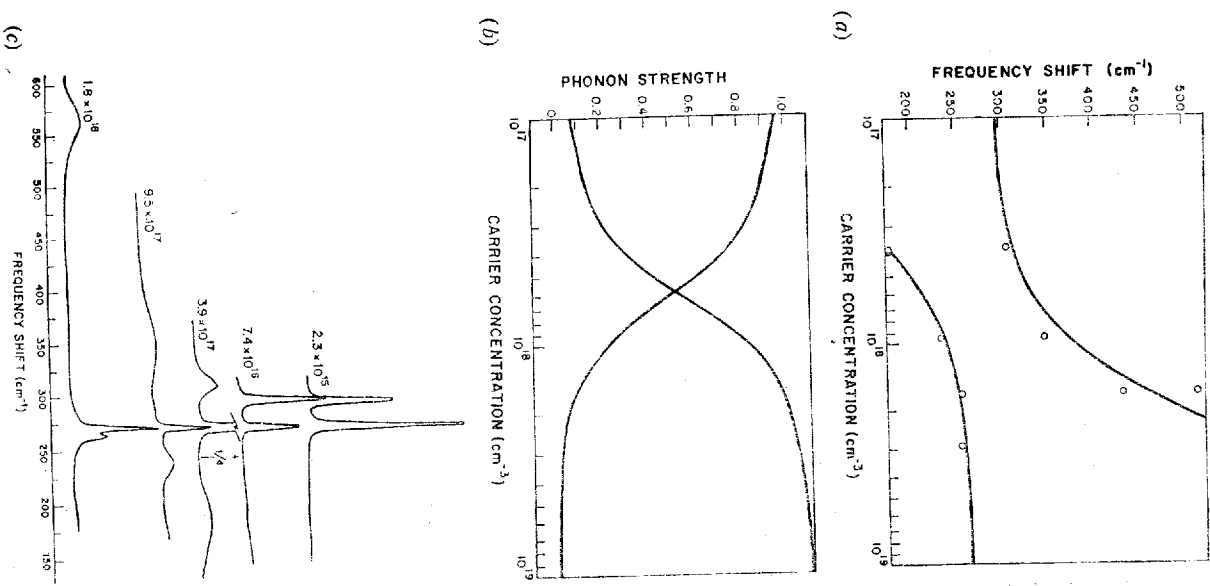


Fig. 9. Experimental illustration of coupled modes. Because the longitudinal optical mode in GaAs is coupled to the plasma mode according to Eq. (46), variation of the carrier concentration, n , and hence the plasma frequency $\omega_p^2 = [11.4 \times 10^{-14} n] \text{ cm}^{-2}$ alters (a) the frequencies of the coupled modes ω_1 and ω_2 , and (b) the strength, Z_1 , of each mode. The other constants in Eq. (46) are $c = [1.29 \times 10^5] \text{ cm}^{-2}$ and $\omega_l = 291 \text{ cm}^{-1}$. In (c) some typical tracings are shown.

The simple model we have been discussing is not as experimentally accessible as some more complicated examples. The three dimensional analog, however, is exemplified by the motion of tagged particle (the oscillator) in a fluid (say a noble liquid) and this motion, self diffusion, is accessible to neutron studies. Actually, the most reliable "measurement" of it are not these neutron studies but computer studies^{7,8} in which the average properties of a particle in the fluid are determined by computing the dynamical behavior of particles interacting by van der Waals forces. The quantity, $\omega\chi''(\omega)$, is exhibited for one value of the temperature and density in argon in Fig. 11. Also plotted⁹ in Fig. 12 are the functions $\gamma'(\omega)$ and its Fourier transform $\tilde{\gamma}'(t-t')$. Plotted for comparison on the same graphs are the Drude or Maxwell fit single collision time model, as obtained by Rice,¹⁰ on the basis of rather more formidable arguments than Drude or Maxwell would ascribe to such an interpolation procedure.

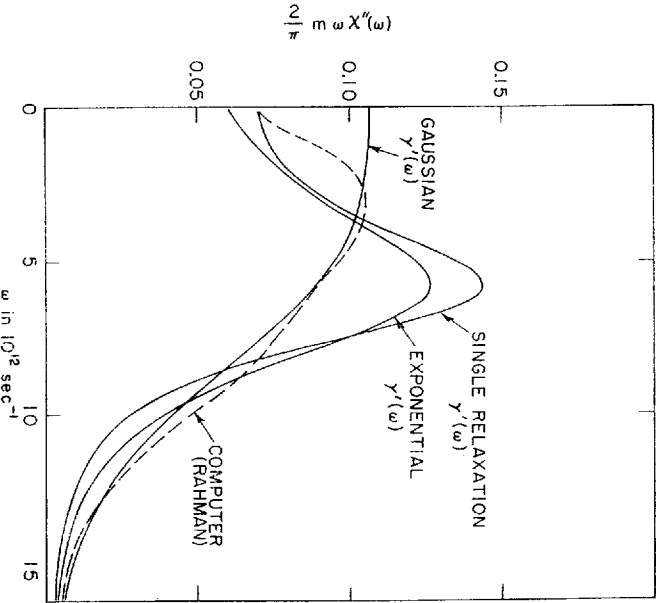


Fig. 11. The absorptive response, χ'' , as determined by computer studies on liquid argon and various fits in terms of phenomenological laws described by simple functions $\gamma''(\omega)$.

A second physical example, involving only oscillators, is the most simplified version of the localised mode problem, a particle with a different mass but the same spring constant placed in a crystal which we idealize

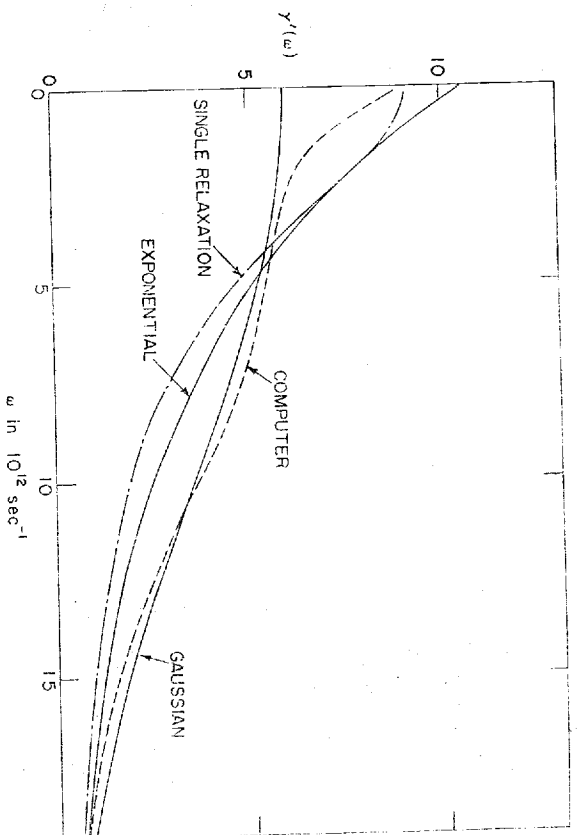


Fig. 12a. The actual phenomenological function, γ' , determined from the computer studies and the fits.

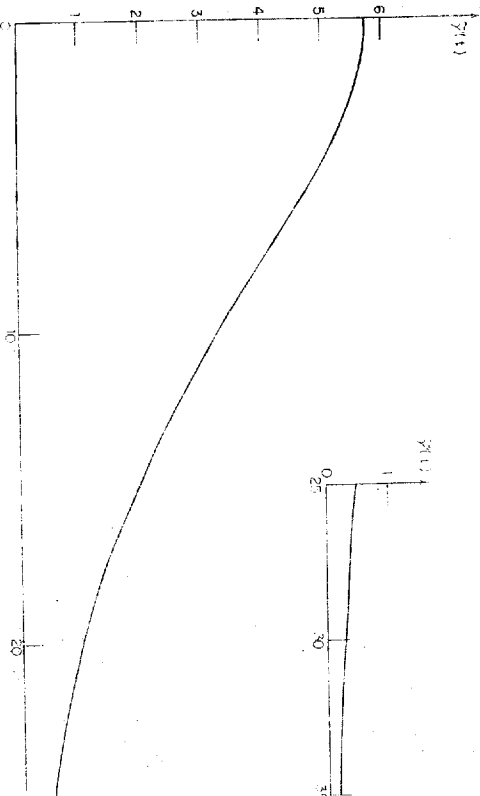


Fig. 12b. The phenomenological function $\tilde{\gamma}'(t)$ whose transform is $\gamma'(\omega)$.

by a linear chain.¹¹ The Hamiltonian for this system may be written as

$$H = \sum_{\alpha} \frac{p_{\alpha}^2}{2\bar{m}} + \frac{\bar{m}}{2} \sum \omega_{0,\alpha\beta}^2 x_{\alpha} x_{\beta} - \frac{p_0^2}{2\bar{m}} \frac{\delta m}{m}; \quad \delta m = m - \bar{m} \quad (47)$$

where x_0 is the coordinate of the tagged particle whose mass is m . The equations of motion are

$$\bar{m}\ddot{x}_\alpha + \sum_\beta \bar{m}\omega_{\alpha\beta}^2 x_\beta + \sum (\delta m) \delta_{\alpha\delta} \delta_{\beta\delta} \dot{x}_\beta = 0. \quad (48)$$

By the same technique employed earlier we have

$$\sum_\beta (-\bar{m}z^2 \delta_{\alpha\beta} + \bar{m}\omega_{\alpha\beta}^2 - \delta m z^2 \delta_{\alpha\delta} \delta_{\beta\delta}) \chi_{\beta\gamma}(z) = \delta_{\alpha\gamma}. \quad (49)$$

This is a matrix equation for the matrix χ , whose inverse is

$$\begin{aligned} [\chi^{-1}(z)]_{\alpha\beta} &= -\bar{m}(z^2 \delta_{\alpha\beta} - \omega_{\alpha\beta}^2) - \delta m z^2 \delta_{\alpha\delta} \delta_{\beta\delta} \\ &= [\chi^{-1}(z; \delta m = 0)]_{\alpha\beta} - \delta m z^2 \delta_{\alpha\delta} \delta_{\beta\delta}. \end{aligned} \quad (50)$$

Let us denote the matrix $\chi(z; \delta m = 0)$ as $\chi^0(z)$. Then we have

$$\chi_{\alpha\beta}(z) = \chi_{\alpha\beta}^0(z) - \delta m z^2 \chi_{\alpha\delta}^0(z) \chi_{\delta\beta}^0(z).$$

Since this equation implies that

$$\chi_{0\beta}(z) = \chi_{0\beta}^0(z) + \delta m z^2 \chi_{0\delta}^0(z) \chi_{\delta\beta}^0(z)$$

we have

$$\chi_{\alpha\beta}(z) = \chi_{\alpha\beta}^0(z) + \delta m z^2 \chi_{\alpha\delta}^0(z) [1 - \delta m z^2 \chi_{\delta\delta}^0(z)]^{-1} \chi_{\delta\beta}^0(z),$$

and in particular,

$$\chi_{00}(z) = \chi_{00}^0(z) [1 - \delta m z^2 \chi_{00}^0(z)]^{-1}. \quad (51)$$

The quantity $\chi_{00}(z)$ is the correlation function $\chi(z)$ for the selected particle. We have for its correlation function

$$\chi^{-1}(z) = \chi^0{}^{-1}(z) - \delta m z^2 \equiv -m[z^2 + iz\gamma(z)]. \quad (52)$$

Let us also introduce the symbol (in a notation which we will understand better a little later),

$$\bar{m}\chi_{sv}^0(z) \equiv \bar{m}z^2 \chi^0(z) + 1;$$

$$\chi_{sv}^0(\omega) = \chi_{sv}^0{}'(\omega) + i\chi_{sv}^0{}''(\omega);$$

$$\chi_{sv}^0{}''(\omega) = \omega^2 \chi^0{}''(\omega); \quad \chi_{sv}^0{}'(\omega) = P \int \frac{d\omega'}{\pi} \frac{\chi_{sv}^0{}''(\omega')}{\omega' - \omega}.$$

Then our equation for $\chi(z)$ reduces to

$$\delta m \chi(z) = \bar{m} \chi^0(z) [\bar{m}/\delta m] + 1 - \bar{m} \chi_{sv}^0(z)]^{-1}. \quad (53)$$

In this equation all the dependence on m occurs through the explicit δm ; the quantity $\bar{m}\chi_{sv}^0(z)$ is independent of m . The dependence on m can therefore be readily examined. A resonance in $\chi(z)$ will occur when the real part of the bracketed expression vanishes and the imaginary part is slowly varying over the width. The resonance will be infinitely sharp (a local mode)

if the imaginary part vanishes where the real part does (which will be the case when m is sufficiently small). For larger m , but m which are still considerably smaller than \bar{m} and again for $m \gg \bar{m}$, there will be a resonance, in the first case near the top of the band, in the second near the bottom. When $m \sim \bar{m}$ there is no resonance nor significant difference between χ'' and $\chi^0{}''$. In Fig. 13a the behavior of $\bar{m}\chi_{sv}^0(\omega)$ and $\bar{m}\chi_{sv}^0{}''(\omega)$ is plotted together with

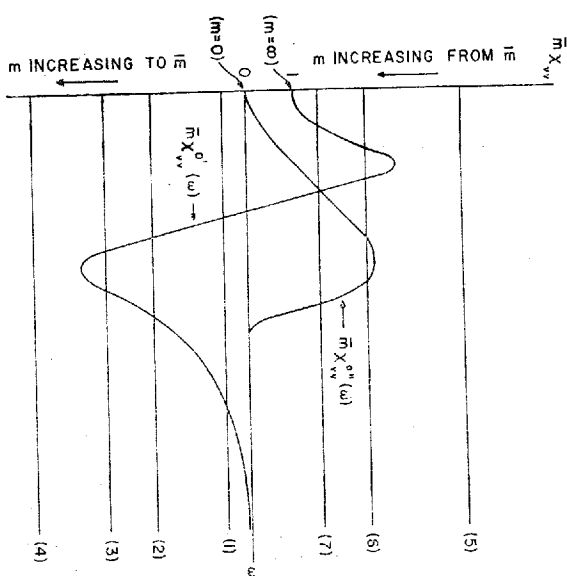


Fig. 13a. The spectrum of the perfect crystal. A plot of $\bar{m}\chi_{sv}^0(\omega)$ and $\bar{m}\chi_{sv}^0{}''(\omega)$. Also plotted are horizontal lines corresponding to different possible values for $[1 + \bar{m}/\delta m]$. Only with (1) does the intercept occur outside the continuum.

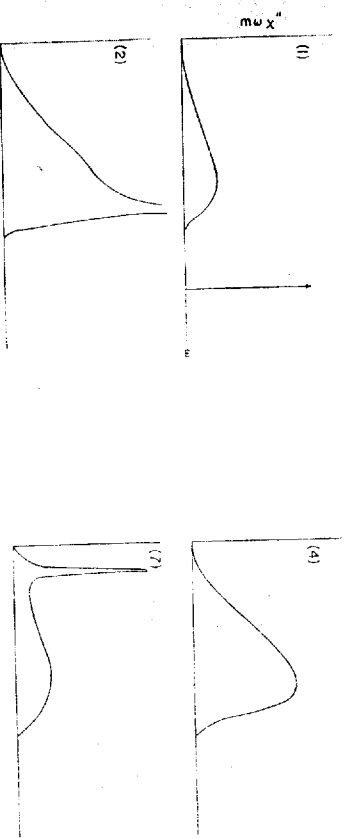


Fig. 13b. The spectrum of the particle of differing mass. In the situation, (1), a local mode occurs. When $m \cong \bar{m}$, (3) -- (6) nothing dramatic happens. In other situations (2) and (7), a resonance occurs. Qualitative graphs of $m\omega\chi''(\omega)$ corresponding to the various intercepts in Fig. 13a are shown.

$(\bar{m}/\delta m + 1)$ and in Fig. 13b the resultant $m\omega\chi''(\omega)$ is plotted for various values of m . The analytical expression these curves describe is

$$\chi''(\omega) = \frac{\bar{m}^2 \chi^{0''}(\omega)}{(\delta m)^2} \left\{ \left(1 + \frac{\bar{m}}{\delta m} - \bar{m} \chi_{av}^{0''}(\omega) \right)^2 + (\bar{m} \chi_{av}^{0''}(\omega))^2 \right\}^{-1} \quad (54)$$

B. Formal Development

Having illustrated various phenomena in term of this simple model, let us consider these arguments from a more general and rigorous point of view.¹² In this microscopic discussion, which we shall carry out quantum mechanically, the first and most important observation we wish to make concerns the rigorous identification of $\chi''(t-t')$ with an equilibrium correlation function, a commutator (classically it would be a Poisson bracket). Having made this identification we may systematically examine its properties—notably symmetries, sum rules, and dispersion relations. We shall for example, see that the statement

$$\int \frac{d\omega}{\pi} \chi''(\omega) \omega = \frac{1}{m}$$

is just the statement

$$\left\langle \frac{i}{\hbar} [x(t), x(t')] \right\rangle_{\text{eq.}} = \frac{i}{m\hbar} \left\langle [p(t), x(t')] \right\rangle_{\text{eq.}} = \frac{1}{m}.$$

From this microscopic viewpoint, the unproven statements we made earlier about function $\chi''(\omega)$ will emerge. In particular, we shall deduce the Nyquist theorem.

1. Time Dependent Perturbation Theory

We turn first to a general classical or quantum mechanical description of the effect of applying a weak external disturbance to a steady state. In mathematical terms, we suppose that prior to time t_0 the system is described by a density matrix, ρ , which commutes with the time independent Hamiltonian H_0 . Subsequent to t_0 an external disturbance is applied which couples to the observable properties, $A_j(\mathbf{r}_i)$, of the system. We describe this disturbance by an additional term in the Hamiltonian

$$H_{\text{ext}}(t) = - \int d\mathbf{r} \sum_j A_j(\mathbf{r}_i) a_j(\mathbf{r}_i). \quad (1)$$

The functions $a_j(\mathbf{r}_i)$ represent the generalized external forces. For example, the observables might include components of the magnetization, in which case the corresponding forces a_j would be the components of the external magnetic field. For our oscillator $A(\mathbf{r}_i) \rightarrow x(t)$ and $a(\mathbf{r}_i) \rightarrow F^{\text{ext}}(t)$. To calculate the expectation value at time t of the observable A_i we must

calculate

$$\text{Tr}[\rho A_i(\mathbf{r}_i)] \equiv \langle A_i(\mathbf{r}_i) \rangle_{n.e.} \quad (2)$$

where ρ is the density matrix. Let us suppose for simplicity, that A does not depend on the time explicitly but only through the dynamical variables. We may either look upon (2) in the Heisenberg picture, in which the observable $A(\mathbf{r}_i)$ changes in time because the dynamical variables on which it depends evolve and the density matrix is unaltered, or in the Schrödinger picture in which $A(\mathbf{r}_i)$ is time independent but the dependence of the dynamical variables on t is accounted for by the time evolution of the density matrix. Independent of which picture we prefer we may write

$$\langle A_i(\mathbf{r}_i) \rangle_{n.e.} = \text{Tr}[\rho U^{-1}(t_0) A_i(\mathbf{r}_i) U(t_0)] \quad (3)$$

where $U(t_0)$ is the unitary operator which describes the way the system changes in time and satisfies the Schrödinger equation

$$i\hbar \frac{d}{dt} U(t_0) = (H_0 + H_{\text{ext}}(t)) U(t_0)$$

with the initial condition

$$U(t_0, t_0) = 1.$$

If we let

$$U(t_0) = U_0(t_0) U'(t_0)$$

where U_0 satisfies $i\hbar \frac{d}{dt} U_0 = H_0 U_0$ we obtain

$$i\hbar \frac{d}{dt} U'(t_0) = [U_0^{-1}(t_0) H_{\text{ext}}(t) U_0(t_0)] U'(t_0)$$

$$i\hbar \frac{d}{dt} U'(t_0) \equiv H_{\text{ext}}^I(t) U'(t_0)$$

whose solution is

$$\begin{aligned} U'(t_0) &= 1 + \frac{1}{i\hbar} \int_{t_0}^t H_{\text{ext}}^I(t') dt' + \left(\frac{1}{i\hbar}\right)^2 \int_{t_0}^t \int_{t_0}^{t'} H_{\text{ext}}^I(t'') dt'' \int_{t_0}^{t'} H_{\text{ext}}^I(t''') dt''' + \dots \\ &\equiv T \left[\exp \left(\frac{1}{i\hbar} \int_{t_0}^t H_{\text{ext}}^I(t') dt' \right) \right]. \end{aligned} \quad (4)$$

If we denote by $A^I(\mathbf{r}_i)$, the Heisenberg operators for the Hamiltonian H_0 , i.e.

$$A_i^I(\mathbf{r}_i) = U_0^{-1}(t_0) A_i(\mathbf{r}_i) U_0(t_0) \quad (5)$$

then we may write

$$\begin{aligned} \text{Tr}[\varrho U^{-1} A_i(\mathbf{r}; t_0) U] &= \text{Tr}[\varrho U^{t-t_0-1} A_i^t(\mathbf{r}; t) U^t] \\ &= \text{Tr} \left[\varrho \left\{ A^t + \frac{i}{\hbar} \sum_j \int d\mathbf{r}' \int_{t_0}^t dt' [A_i^t(\mathbf{r}; t), A_j^t(\mathbf{r}'; t')] a_j(\mathbf{r}'; t') \right\} + \dots \right] \end{aligned}$$

or, with the understanding that when there are no superscripts I , we are discussing the steady state density matrix commuting with H_0 and operators which evolve according to it,

$$\langle A_i(\mathbf{r}; t) \rangle_{n.e.} \cong \langle A_i(\mathbf{r}; t) \rangle + \frac{i}{\hbar} \sum_j \int d\mathbf{r}' \int_{t_0}^t dt' \langle [A_i(\mathbf{r}; t), A_j(\mathbf{r}'; t')] \rangle a_j(\mathbf{r}'; t') + \dots \quad (6)$$

We now define the absorptive response as the commutator

$$\tilde{\chi}_{ij}''(\mathbf{r}'; t-t') \equiv \frac{1}{2\hbar} \langle [A_i(\mathbf{r}; t), A_j(\mathbf{r}'; t')] \rangle \quad (7)$$

$$= \int \frac{d\omega}{2\pi} e^{-i\omega(t-t')} \chi_{ij}''(\mathbf{r}'; \omega). \quad (8)$$

In terms of χ'' and the step function $\eta(t-t')$ we may write

$$\langle A_i \rangle - \langle A_j \rangle \cong \delta \langle A_i(\mathbf{r}; t) \rangle = \sum_j \int d\mathbf{r}' \int_{-\infty}^{\infty} 2dt' \tilde{\chi}_{ij}''(\mathbf{r}'; t-t') a_j(\mathbf{r}'; t') \eta(t-t') \quad (9)$$

The corresponding classical expression is

$$\delta A_i(\mathbf{r}; t) = - \sum_j \int_{t_0}^t \langle [A_i(\mathbf{r}; t), A_j(\mathbf{r}'; t')] \rangle_{P.B.} a_j(\mathbf{r}'; t')$$

which leads us to define

$$\chi_{ij}''^{cl} = \frac{i}{2} \langle [A_i(\mathbf{r}; t), A_j(\mathbf{r}'; t')] \rangle_{P.B.}$$

(Being more explicit requires unfortunately complicated notation, i.e.,

$$\chi_{ij}''^{cl} = \frac{i}{2} \left\langle \sum_{\alpha} \frac{\partial A_i(\mathbf{r}; t)}{\partial p_{\alpha}(t)} \frac{\partial A_j(\mathbf{r}'; t')}{\partial p_{\alpha}(t')} - \frac{\partial A_i(\mathbf{r}; t)}{\partial p_{\alpha}(t)} \frac{\partial A_j(\mathbf{r}'; t')}{\partial r_{\alpha}(t')} \right\rangle$$

with $\partial A_i(\mathbf{r}; t) / \partial p_{\alpha}(t) \equiv \partial A_i(\mathbf{r}; t) / \partial p_{\alpha}(t)$, $\partial A_i(\mathbf{r}; t) / \partial r_{\alpha}(t) \equiv \partial A_i(\mathbf{r}; t) / \partial r_{\alpha}(t)$, the derivative at time t with respect to the dynamical variable into which the variable at the common time t' has evolved under the hamiltonian H_0 . This value is classically determined by the Liouville operator L_0 associated with H_0 by the above expression.) To prove the classical version, we recall that if the system is described classically by a distribution function

$f = f(\mathbf{r}; \alpha(t), p_{\alpha}(t))$, we may write to first order

$$\begin{aligned} f &= f_0 + \sum_{\alpha} \left(\delta r^{\alpha}(t) \frac{\partial}{\partial r^{\alpha}(t)} + \delta p^{\alpha}(t) \frac{\partial}{\partial p^{\alpha}(t)} \right) f_0 \\ \delta f &= \sum_{\alpha} \left[\int_{t_0}^t dt' \delta v^{\alpha}(t') \frac{\partial}{\partial r_0^{\alpha}(t')} + \int_{t_0}^t dt' F_{\text{ext}}^{\alpha}(t') \frac{\partial}{\partial p_0^{\alpha}(t')} \right] f_0 \\ &= \int_{t_0}^t [L_0(t'), H_{\text{ext}}(t')]_{P.B.} dt'. \end{aligned}$$

This expression, like the one for the perturbed quantum mechanical density matrix, is only useful for calculating expectation values of operators for generic measurable quantities—functions of a few variables symmetrical in the many coordinates of the system and not distinguishing among them. For these quantities, we have

$$\delta \langle A_i(\mathbf{r}; t) \rangle = \sum_j \int_{t_0}^t \langle [A_i(\mathbf{r}; t), A_j(\mathbf{r}'; t')] \rangle_{P.B.} a_j(\mathbf{r}'; t') dr' dt'$$

where as usual, the brackets indicate an ensemble average.

We now define

$$\tilde{\chi}_{ij}(\mathbf{r}'; t-t') \equiv 2i\eta(t-t') \tilde{\chi}_{ij}''(\mathbf{r}'; t-t') \quad (10)$$

$$\delta \langle A_i(\mathbf{r}; t) \rangle = \sum_j \int d\mathbf{r}' \int_{-\infty}^{\infty} dt' \tilde{\chi}_{ij}(\mathbf{r}'; t-t') a_j(\mathbf{r}'; t'). \quad (9')$$

The function $\tilde{\chi}_{ij}(\mathbf{r}'; t-t')$ is the Fourier transform of the complex response $\chi_{ij}(\mathbf{r}'; \omega)$. Moreover,

$$\chi_{ij}(\mathbf{r}'; \omega) = \chi_{ij}'(\mathbf{r}'; \omega) + \chi_{ij}''(\mathbf{r}'; \omega) \quad (11)$$

is the boundary value as z approaches ω on the real axis from above, of the analytic function of z

$$\chi_{ij}(\mathbf{r}'; z) = \int \frac{d\omega'}{\pi} \frac{\chi_{ij}''(\mathbf{r}'; \omega')}{\omega' - z}. \quad (12)$$

It follows immediately from these equations that χ' and χ'' satisfy Kramers-Kronig relations,

$$\chi_{ij}'(\mathbf{r}'; \omega) = P \int \frac{d\omega'}{\pi} \frac{\chi_{ij}''(\mathbf{r}'; \omega')}{\omega' - \omega}; \quad \chi_{ij}''(\mathbf{r}'; \omega) = -P \int \frac{d\omega'}{\pi} \frac{\chi_{ij}'(\mathbf{r}'; \omega')}{\omega' - \omega}. \quad (13)$$

2. Symmetry Properties of the Response Function

(i) Since χ_{ij}'' is a commutator, it is antisymmetric under interchange of \mathbf{r} with \mathbf{r}' , i with j , and t with t' . We therefore have

$$\begin{aligned} \tilde{\chi}_{ij}''(\mathbf{r}'; t-t') &= -\tilde{\chi}_{ji}''(\mathbf{r}; t'-t) \\ \chi_{ij}''(\mathbf{r}'; \omega) &= -\chi_{ji}''(\mathbf{r}; -\omega). \end{aligned} \quad (14)$$

