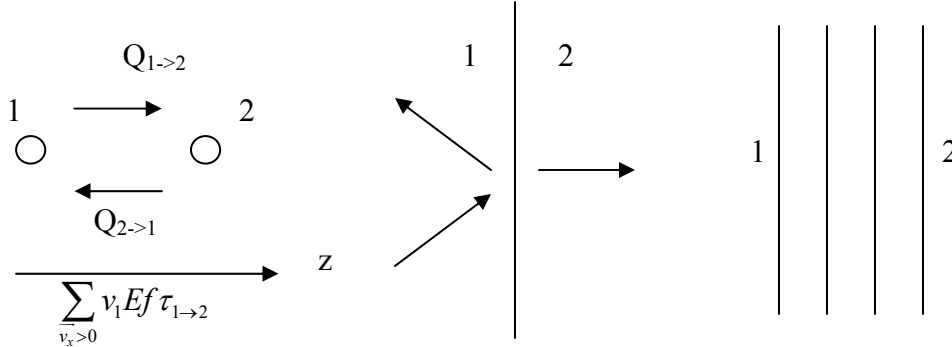


2.57 Nano-to-Macro Transport Processes
Fall 2004
Lecture 16

Review of last lecture

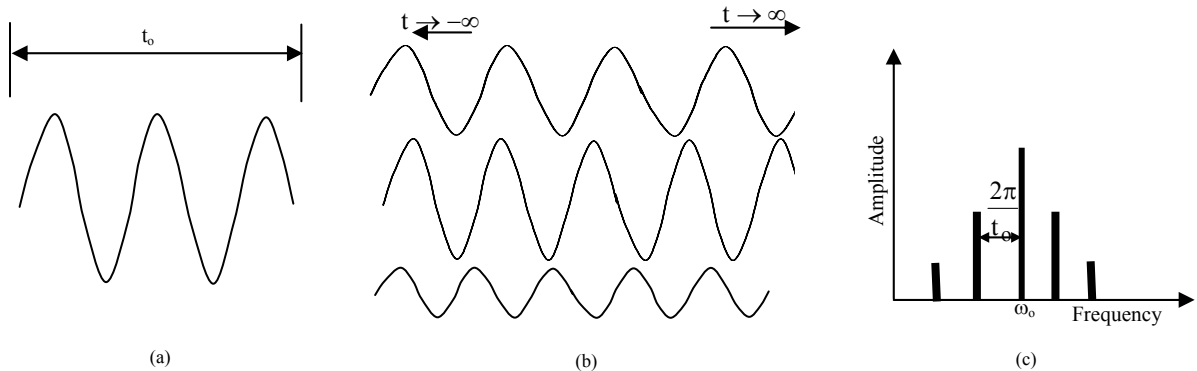


In Lecture 14, we have discussed the energy exchange between two points. We have spent time on calculating the transmissivity $\tau_{1 \rightarrow 2}$ for cases in the right two figures. The velocity v_1 is the group velocity, not the phase velocity determined by $v = \omega / k_x$ (derived from constant phase $\Phi = \omega t - k_x x$.)

Consider a plane traveling along x-direction

$$\mathbf{A}e^{-i(\omega t - kx)}$$

The velocity $v = \omega / k_x$ is NOT the speed of signal or energy propagation. We see that the plane wave represented by above equation extends from minus infinite to plus infinite in both time and space. There is no start or finish and it does not represent any meaningful signal. In practice, a signal has a starting point and an ending point in time. Let's suppose that a harmonic signal at frequency ω_0 is generated during a time period $[0, t_0]$, as shown in the following figure (a).



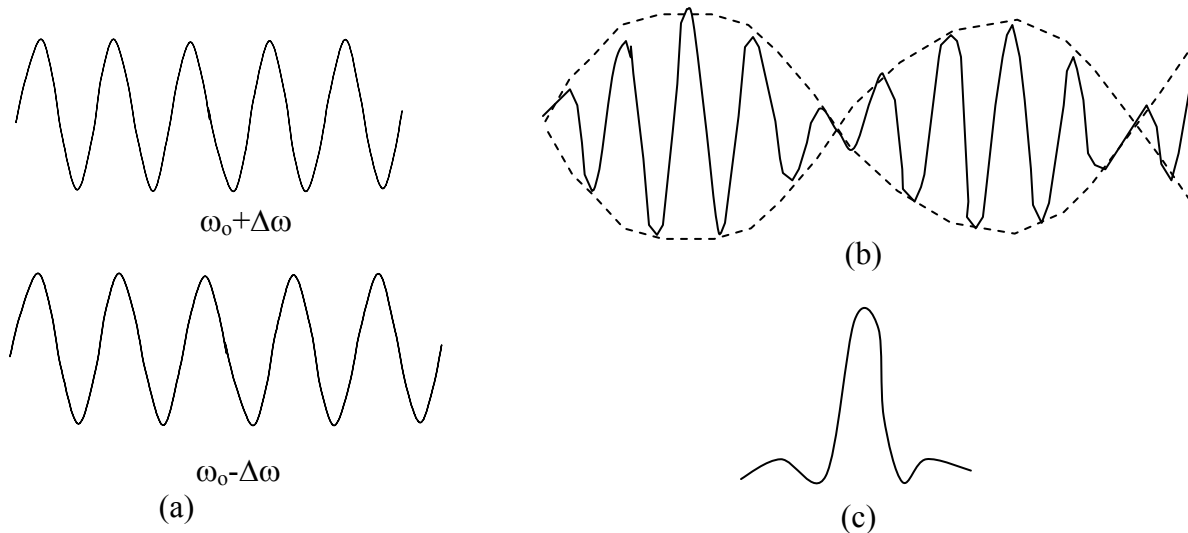
Such a finite-time harmonic signal can be decomposed through Fourier series into the summation of truly plane waves with time extending from minus infinite to plus infinite, as shown in figure (b). The frequencies of these plane waves are centered around ω_0 and their amplitudes decay as frequency moves away from ω_0 , as illustrated in figure (c).

One can better understand these pictures by actually carrying out the Fourier expansion ($\sum a_n \sin \frac{2\pi n}{T} t$). Because each of the plane waves in such a series expansion is at a frequency slight different from the central frequency ω_0 , it also has a corresponding wavevector that is different from k_0 , as determined by the dispersion relation between $\omega(k)$. The subsequent propagation of the signal can be obtained from tracing the spatial evolution of all these Fourier components as a function of time.

For simplicity, let's consider that the signal is an electromagnetic wave. We pick up only two of the Fourier components and consider their superposition, one at frequency $\omega_0 - \Delta\omega/2$ and another at frequency $\omega_0 + \Delta\omega/2$ propagating along positive x-direction [figure (a)]. The superposition of these two waves gives the electric fields as

$$E_y(x,t) = a \exp\{-i[(\omega_0 - \Delta\omega)t - (k_0 - \Delta k)x]\} + a \exp\{-i[(\omega_0 + \Delta\omega)t - (k_0 + \Delta k)x]\}$$

$$= 2a \cos(\Delta\omega \cdot t - \Delta k \cdot x) \exp[-i(\omega_0 t - k_0 x)]$$



The electric field is schematically shown in above figures. There appears to be two waves, one is the carrier wave at central frequency ω_0 (term $\exp[-i(\omega_0 t - k_0 x)]$), another is the modulation of the carrier wave by a wave at frequency $\Delta\omega$ (the amplitude term $2a \cos(\Delta\omega \cdot t - \Delta k \cdot x)$ in $E_y(x,t)$). The latter one changes much slower compared with the former one.

Note: (1) In the product $\Psi \nabla \Psi^*$ for flux J, the exponential term $\exp[-i(\omega_0 t - k_0 x)]$ is cancelled out. The time influence only exists in $2a \cos(\Delta\omega \cdot t - \Delta k \cdot x)$. (2) We need to calculate the time-averaged Poynting vector $\frac{1}{2} \text{Re}(\vec{E} \times \vec{H}^*)$ to get the real energy flux. This yields another wave propagating at the speed

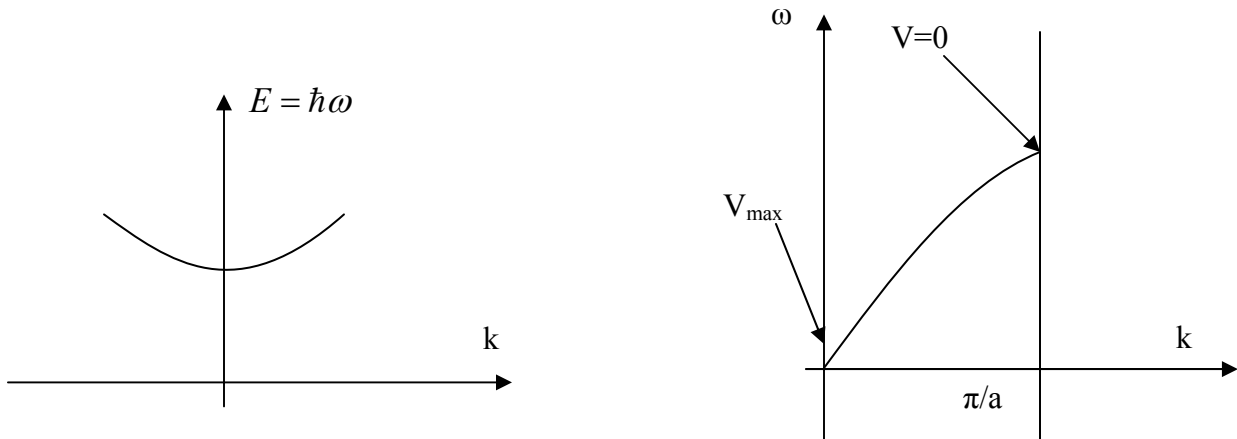
$$v_{g,x} = \frac{\Delta\omega}{\Delta k} = \frac{d\omega}{dk},$$

which means that the energy is propagating at the speed of $v_{g,x}$ rather than the phase velocity. We can also find this velocity from $\Delta\omega \bullet t - \Delta k \bullet x = 0$ in $E_y(x,t)$. This v_g is called the group velocity. In the more general case of the existence of a spectrum of frequencies, the superposition of waves leads to a narrow **wave packet** as sketched in above figure (c). The group velocity can be calculated from

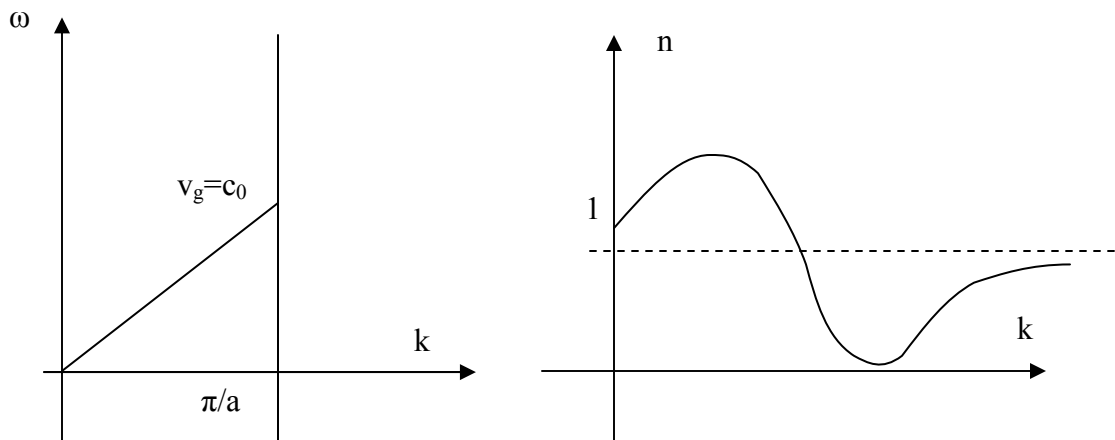
$$\mathbf{v}_g = \nabla_{\mathbf{k}} \omega = \frac{\partial \omega}{\partial k_x} \hat{k}_x + \frac{\partial \omega}{\partial k_y} \hat{k}_y + \frac{\partial \omega}{\partial k_z} \hat{k}_z.$$

Discussions

(1) In the following left figure, electrons in the conduction band have different group velocities (gradient in all figures) at different wave vectors. This is also the case for phonons, as shown in the right figure.

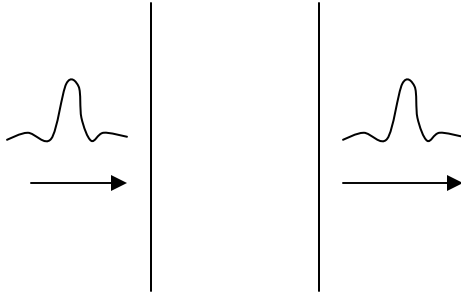


For photons, the group velocity is constant (the following left figure).



(2) In most cases, the energy velocity is just the group velocity. However, for photons the group velocity can be larger than the speed of light in special cases. We can appreciate this from the calculation of Poynting vector, where we assumed that $\Delta\omega$ is much smaller

than ω_0 . In the case of a very large variation in the dispersion relation, the group velocity no longer represents the energy velocity. Suppose we have a material with refractive index $n(\omega)$ changing rapidly with wavelength, also drawn as a function of k in the above right figure. The speed of light inside the material is $c = \frac{c_0}{n(\omega)}$. In a region, the real part of the refractive index is less than 1 and the phase velocity is larger than the speed of light. The front of the wave packet also moves with a speed larger than c_0 . This paradox is explained by noticing the majority energy still lies in the part behind the wave front. Therefore, the real energy speed is smaller than the speed of light.



Brillouin wrote his thesis on the group, signal velocities. For personal interests, you may want to read it for better understanding.

(3) The group velocity of electrons is velocity at which the electron wave packets moves in free space and inside a crystal. The energy dispersion of a free electron is

$$E = \frac{(\hbar\mathbf{k})^2}{2m}$$

and thus the phase and group velocity are, respectively,

$$\mathbf{v} = \frac{E/\hbar}{\mathbf{k}} = \frac{\hbar\mathbf{k}}{2m} \quad \text{and} \quad \mathbf{v}_g = \frac{\partial(E/\hbar)}{\partial\mathbf{k}} = \frac{\hbar\mathbf{k}}{m}$$

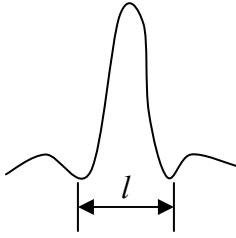
Clearly, the group velocity is consistent with the de Broglie relation $\mathbf{p} = \hbar\mathbf{k}$ and our classical relation $\mathbf{p} = m\mathbf{v}_g$, but not the phase velocity.

5.6.2 Loss of coherence

(1) Inelastic scattering

The scattering of electrons can be **elastic** in which the electrons merely change directions but have the same energy before and after the scattering, or **inelastic** in which both direction and energy of electrons are changed. The scattering of electrons by impurities and at the boundaries is elastic. The elastic scattering itself does not destroy the phase but the random locations of the impurities and the surface roughness, may create enough randomness in the phase such that the particle approach is approximately valid, or in other cases, the randomness can also create localization of the electron waves. The inelastic scattering, such as electron-phonon scattering, however, randomizes the phases because the location and the phase of the electron-phonon scattering change all the time.

In our previous discussion of transmissivity, we did not include the inelastic scattering and treat it as particle transport instead of using phase of wave functions.



For the above wave packet, the coherence length is defined as

$$l \sim \frac{V}{\Delta \nu},$$

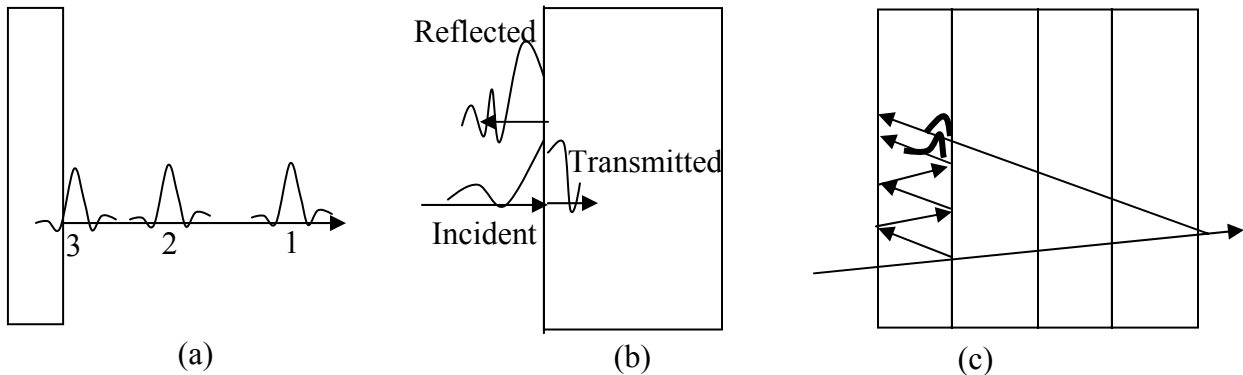
where $\Delta \nu$ is determined by $2\Delta\omega$ in the foregoing discussion. For lasers, $\Delta \nu$ is small and l can be on the magnitude of kilometers.

Now let us estimate the coherence length of blackbody radiation. The energy uncertainty of the individual radiation emitters (atoms, electrons, or molecules) is of the order of $k_B T$ due to the collision of the emitters with the reservoir, which also means that the effective bandwidth for thermal emission is $\Delta \nu = k_B T / h$. Using this effective bandwidth, one can

estimate that the coherence length $\sim hc / (k_B T) = \frac{3E8 * 6.6E-34}{1.38E-23 * 300} = 3E-5$, which corresponds to $l_c T = 2167.8 \mu\text{m.K}$, very close to the Wien's displacement law.

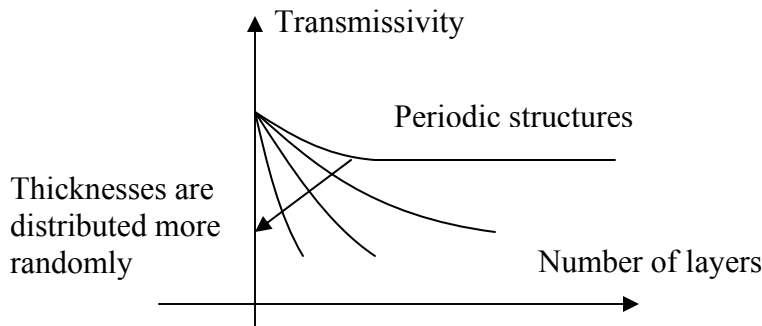
For electrons, $l_c = 100\text{-}1000 \text{ \AA}$, while it is $1\text{-}10 \text{ \AA}$ for phonons.

2) Spatial & temporal coherence



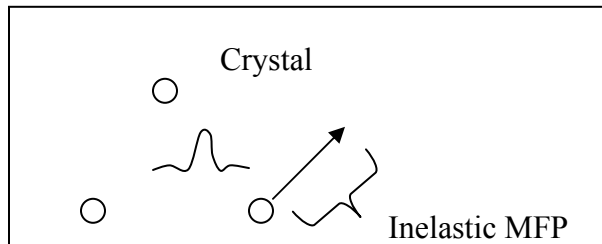
The coherence length as a measure of the wave packet size gives an indication whether the phase information needs to be considered for the transport processes or not. If the size of the transport domain is much larger than the wave packets or the coherence length, than the wave packets can be treated as point-wise particles traveling through the domain, as shown in above figure (a). When a wave packet meets a perfect interface, however,

the wave packet will be reflected and refracted. The refracted wave packet has a fixed phase relationship with the incoming one and can thus interfere with the incoming wave packet [figure (b)]. This is the reason why we always use Fresnel formula---the wave solution of the Maxwell equations, to calculate the interface reflectivity and transmissivity of a perfect interface. In the case of multilayers, there is still overlap between the incoming and reflected wave packet even if the layer is very thick [figure (c)]. If we alter the thickness of each layer randomly, the overlap still exists. The transmissivity is drawn in the following figure.

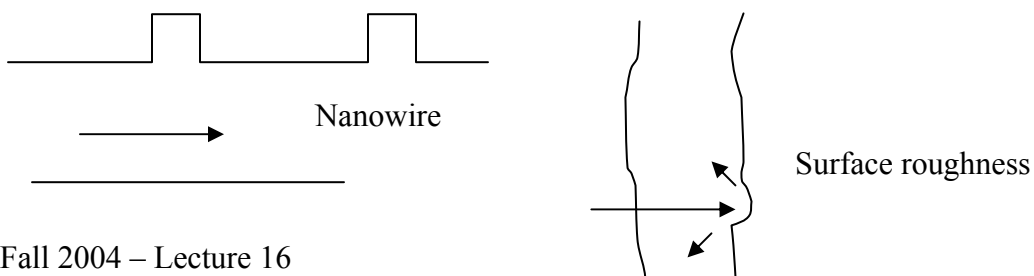


Note: Randomly distributed thickness will cause localization phenomena and reduce the transmissivity, which won Phillip Anderson a Nobel Prize in physics.

Consider scattering in the following crystal. The wave is scattered at random points due to inelastic scattering such as by phonons. In this case, we can ignore the phase information and the particle picture is valid.



When size effects appear, the characteristic length is normally less than the inelastic mean free path. This can be the case for nanowires. However, the particle treatment may be still valid due to the boundary scattering. Although boundary scattering is not random and most likely elastic, the roughness diffracts waves into all directions. The averaging of the diffracted waves usually leads to results more closely to particle treatment than these based ideal interfaces. For phonons in a film with surface roughness, we can argue in the same way.

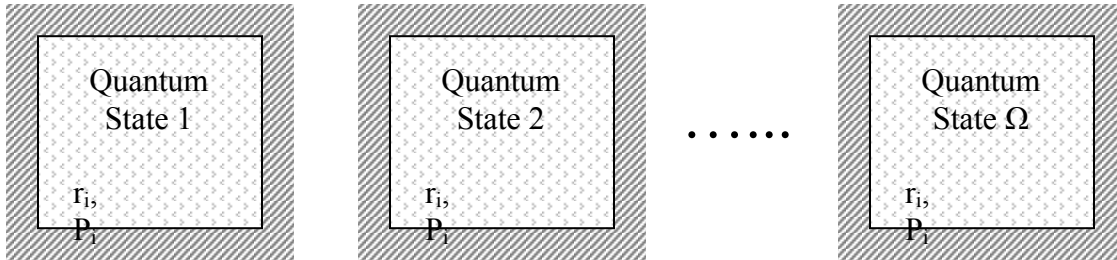


Chapter 6 Particle Description of Transport Process

6.1 Liouville equation and Boltzmann equation

In chapter 4, we studied systems at equilibrium and developed the equilibrium distribution functions $f(E, T, \mu)$ (Fermi-Dirac, Bose-Einstein, and Boltzmann distributions). The distribution function for a quantum state at equilibrium is a function of the energy of the quantum state, the system temperature and chemical potential. When the system is not at equilibrium, these distribution functions are no longer applicable. In the statistical description, we use nonequilibrium distribution functions, which depend not only on the energy and temperature of the system, but also on positions and other variables. We will develop in this chapter the governing equations for the nonequilibrium distribution functions.

In the following figure, we show an ensemble, i.e., a collection of quantum states of a N-particle system.



Now each particle can be described by the generalized coordinate \mathbf{r} and momentum \mathbf{p} . For example, the generalized coordinates of a diatomic molecule, \mathbf{r}_1 , include the position (x_1, y_1, z_1) , the vibrational coordinate (the separation between the two atoms, Δx_1), the rotational coordinates (polar and azimuthal angles, θ_1 and ϕ_1), and the generalized momentum, \mathbf{p}_1 , includes the translational $(mv_{x1}, mv_{y1}, mv_{z1})$, vibrational momentum proportional to the relative velocity of the two atoms $(m d\Delta x_1/dt)$, and rotational momentum (two angular momentum of rotation). We assume here that there are m -degrees of freedom in space, i.e., m generalized spatial coordinates, and m -degrees of freedom in momentum for each particle. The number of the degree of freedom of the whole system is $2n = 2m \times N$. These $2n$ variables form a $2n$ -dimensional space. The system at any instant can be described as one point in such a space. This space is called a phase space. The time evolution of the system, i.e., the time history of all the particles in the system, traces one line in such a $2n$ -dimensional **phase space**, which we will call the flow line as in fluid mechanics.

The number of systems, is

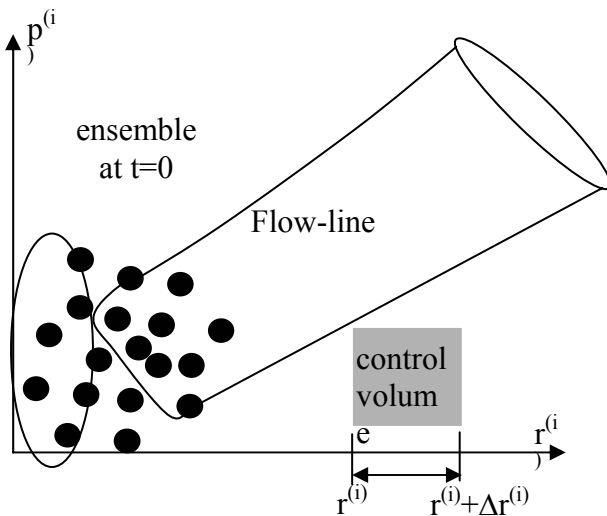
$$\text{No. Systems} = f^{(N)}(\mathbf{t}, \mathbf{r}^{(n)}, \mathbf{p}^{(n)}) \Delta \mathbf{r}^{(n)} \Delta \mathbf{p}^{(n)}$$

in a small volume of the phase space, $\Delta\mathbf{r}^{(n)}\Delta\mathbf{p}^{(n)}$, where $\Delta\mathbf{r}^{(n)}=\Delta r_1\Delta r_2\dots\Delta r_N=\Delta r^{(1)}\Delta r^{(2)}\dots\Delta r^{(n)}$ and $\Delta\mathbf{p}^{(n)}=\Delta p_1\Delta p_2\dots\Delta p_N=\Delta p^{(1)}\Delta p^{(2)}\dots\Delta p^{(n)}$.

The time evolution of $f^{(N)}(t,\mathbf{r}^{(n)},\mathbf{p}^{(n)})$ in the phase space is governed by the **Liouville equation**, which can be derived based on the fact that the traces of systems in the ensemble do not intersect. Consider a tube formed by the traces of a set of points (a subset of systems in the ensemble) as shown in the following figure. Since the flow lines do not intersect, the points in the phase space are conserved. We want to derive an equation for the distribution function f based on this conservation requirement. Recall that in fluid mechanics or heat transfer, we often use the control volume method rather than tracing the trajectory of individual fluid particles. We could do the same for the points in phase space and exam a small control volume in phase space as shown in the figure. The rate of points flow into the control volume should equal to the rate of change inside the control volume. This finally leads to

$$\frac{\partial f^{(N)}}{\partial t} + \sum_{i=1}^n \dot{r}^{(i)} \times \frac{\partial f^{(N)}}{\partial r^{(i)}} + \sum_{i=1}^n \dot{p}^{(i)} \times \frac{\partial f^{(N)}}{\partial p^{(i)}} = 0$$

which is called the Liouville equation.



Note: The Boltzmann equation reduces variables from the Liouville equation, while the linear response theory focuses on small perturbation. They are both simplified form of the Liouville equation.