PHY 770 -- Statistical Mechanics
12:00* - 1:45 PM TR Olin 107

Instructor: Natalie Holzwarth (Olin 300)
Course Webpage: http://www.wfu.edu/~natalie/s14phy770

Lecture 18

Chap. 7 – Brownian motion and other non-equilibrium phenomena

- **Fokker-Planck equation examples**
- **Linear response theory**
- **Fluctuation-Dissipation Theorem**

***Partial make-up lecture -- early start time**

11	Tue: 02/18/2014	Chap. 5	Equilibrium Statistical Mechanics	#11	02/27/2014
12	Thur: 02/20/2014	Chap. 5	The Ising model (class 12-1:45 PM)	#12	02/27/2014
	Tue: 02/25/2014		NAWH out of town -- no class		
13	Thur: 02/27/2014	Chap. 6	Grand partition function (class 12-1:45 PM)		
	Tue: 03/04/2014	*APS Meeting*	Take-home exam (no class meeting)		
	Thur: 03/06/2014	*APS Meeting*	Take-home exam (no class meeting)		
	Tue: 03/11/2014		Spring break (no class meeting)		
	Thur: 03/13/2014		Spring break (no class meeting)		
14	Tue: 03/18/2014	Chap. 6	Fermi and Bose particles (class 12-1:45 PM; Exam due)	#13	03/25/2014
15	Thur: 03/20/2014	Chap. 6	Interacting particles (class 12-1:45 PM)	#14	03/25/2014
16	Tue: 03/25/2014	Chap. 7	Langevin equation (class 12-1:45 PM)	#15	04/01/2014
17	Thur: 03/27/2014	Chap. 7	Fokker-Planck equation (class 12-1:45 PM)	#16	04/03/2014
18	Tue: 04/01/2014	Chap. 7	Linear Response (class 12-1:45 PM)	#17	04/10/2014
19	Thur: 04/03/2014		(class 12-1:45 PM)		
20	Tue: 04/08/2014		(class 12-1:45 PM)		
21	Thur: 04/10/2014		(class 12-1:45 PM)		
22	Tue: 04/15/2014		(class 12-1:45 PM)		
23	Thur: 04/17/2014		(class 12-1:45 PM)		
24	Tue: 04/22/2014		(class 12-1:45 PM)		
	Thur: 04/24/2014		Presentations Part I (class 11-1:45 PM)		
	Tue: 04/29/2014		Presentations Part II (class 11-1:45 PM)		

WFU Joint Physics and Chemistry Colloquium

TITLE: Neutron Scattering Tools for Materials Research

SPEAKER: Dr. Ashfia Huq,

Chemical and Engineering Materials Division,
Spallation Neutron Source, Oak Ridge National Laboratory,
Oak Ridge, TN

TIME: Wednesday April 2, 2014 at 4:00 PM

PLACE: Room 101 Olin Physical Laboratory

Refreshments will be served at 3:30 PM in the Olin Lounge. All interested persons are cordially invited to attend.

ABSTRACT

Historically Oak Ridge National Laboratory has played a very important role in developing neutron scattering techniques for crystallography. Clifford Shull, the winner of the 1994 Noble Prize in Physics started his pioneering work in neutron diffraction in 1946 at Oak Ridge. In keeping with this strong tradition, the lab currently hosts two facilities; High Flux Isotope Reactor and the Spallation Neutron Source, which supports scattering studies in physical, chemical and biological sciences. In this talk I will present an overview of the various different neutron scattering techniques for materials research. A more focused description of neutron powder diffraction will follow with some examples of how this technique has been applied to solve structural questions of some energy related materials.

Probability analysis of Brownian motion -- Fokker-Planck equation

Macroscopic probability: Microscopic probability:

$$P(x,v,t) = \langle \rho(x,v,\xi,t) \rangle_\xi$$

Stochastic force

$$\langle \xi(t_1)\xi(t_2) \rangle_\xi = g\delta(t_1 - t_2)$$

Fokker-Planck equation:

$$\frac{\partial P}{\partial t} = -v\frac{\partial P}{\partial x} + \frac{\partial}{\partial v}\left(\left(\frac{\gamma}{m}v - \frac{1}{m}F(x)\right)P\right) + \frac{g}{2m^2}\frac{\partial^2 P}{\partial v^2}$$

friction coefficient

Conservative force

$$F(x) = \frac{-dV(x)}{dx}$$

Corresponding Langevin equation:

$$\frac{dv(t)}{dt} = -\frac{\gamma}{m}v(t) + \frac{1}{m}F(x) + \frac{1}{m}\xi(t) \qquad v(t) = \frac{dx(t)}{dt}$$

Example solution in the limit of large friction

Langevin equation in presence of friction (γ) and potential force ($F(x) = -\nabla V(x)$):

$$\frac{dv(t)}{dt} = -\frac{\gamma}{m}v(t) + \frac{1}{m}F(x) + \frac{1}{m}\xi(t) \qquad v(t) = \frac{dx(t)}{dt}$$

When γ is sufficiently large, the system reaches a steady-state very rapidly so the $\frac{dv(t)}{dt} \approx 0$ Then the Langevin equation reduces to: $\frac{dx(t)}{dt} = \frac{1}{\gamma}F(x) + \frac{1}{\gamma}\xi(t)$

The Fokker-Planck equation reduces to:

$$\frac{\partial P}{\partial t} = -\frac{\partial}{\partial x}\left(\left(\frac{1}{\gamma}F(x)\right)P\right) + \frac{g}{2\gamma^2}\frac{\partial^2 P}{\partial x^2}$$

Example solution in the limit of large friction -- continued

In this case:

$$\frac{\partial P}{\partial t} = -\frac{\partial}{\partial x}\left(\left(\frac{1}{\gamma}F(x)\right)P\right) + \frac{g}{2\gamma^2}\frac{\partial^2 P}{\partial x^2}$$

Further consider the case where $F(x) = 0$:

$$\frac{\partial P}{\partial t} = \frac{g}{2\gamma^2}\frac{\partial^2 P}{\partial x^2} \equiv D\frac{\partial^2 P}{\partial x^2} \qquad \text{Note: } D = \frac{g}{2\gamma^2} = \frac{2\gamma kT}{2\gamma^2} = \frac{kT}{\gamma}$$

Solution of this diffusion equation:

Let $P(x,t) \equiv \frac{1}{2\pi}\int_{-\infty}^{\infty} dq e^{-iqx}\tilde{P}(q,t)$

$$\frac{\partial \tilde{P}(q,t)}{\partial t} = -q^2 D\tilde{P}(q,t) \qquad \Rightarrow \tilde{P}(q,t) = Ce^{-Dq^2 t}$$

$$P(x,t) \equiv \frac{C}{2\pi}\int_{-\infty}^{\infty} dq e^{-iqx}e^{-Dq^2 t} = \frac{C}{\sqrt{4\pi Dt}}e^{-\frac{x^2}{4Dt}}$$

Example solution for "free" particle *V(x)=0*

Fokker-Planck equation:

$$\frac{\partial P}{\partial t} = -v\frac{\partial P}{\partial x} + \frac{\partial}{\partial v}\left(\left(\frac{\gamma}{m}v + \frac{1}{m}\frac{dV(x)}{dx}\right)P\right) + \frac{g}{2m^2}\frac{\partial^2 P}{\partial v^2}$$

For $V(x) = 0$, we can assume $P(x,v,t) = P(v,t)$

$$\Rightarrow \frac{\partial P}{\partial t} = \frac{\gamma}{m}\frac{\partial(vP)}{\partial v} + \frac{g}{2m^2}\frac{\partial^2 P}{\partial v^2}$$

In order to find solution, define $P(v,t) = e^{-m\gamma v^2/(2g)}\Psi(v,t)$

Let $A \equiv \frac{g}{2\gamma m}$: $\quad \frac{\partial \Psi(v,t)}{\partial t} = \frac{\gamma}{m}\left(\frac{1}{2} - \frac{v^2}{4A} + A\frac{\partial^2}{\partial v^2}\right)\Psi(v,t)$

Example solution for "free" particle *V(x)=0*

$$\text{Note that: } \left(\frac{1}{2}-\frac{v^2}{4A}+A\frac{\partial^2}{\partial v^2}\right)\phi_n(v) = -n\phi_n(v)$$

$$\text{where } \phi_n(v) = \frac{1}{\sqrt{2^n n!\sqrt{2\pi A}}} H_n\left(\frac{v}{\sqrt{2A}}\right)e^{-v^2/(4A)}$$

$$\Rightarrow \Psi(v,t) = \sum_{n=0}^{\infty} a_n e^{-nt\gamma/m}\phi_n(v)$$

$$P(v,t) = e^{-v^2/(4A)}\sum_{n=0}^{\infty} a_n e^{-nt\gamma/m}\phi_n(v)$$

$$\text{For } \quad t\to\infty \quad P(v,t) \approx Ke^{-v^2/(2A)} = Ke^{-m\gamma v^2/g} = Ke^{-mv^2/(2kT)}$$

$$\text{when } \quad g = 2\gamma kT$$

Fluctuations about equilibrium

Consider a Brownian particle of mass m in the presence of random noise $\xi(t)$, fluid friction γ, and an an impulse $F_0\delta(t)$:

$$m\frac{dv}{dt} = -\gamma v(t) + \xi(t) + F_0\delta(t)$$

$$m\frac{d\left\langle v(t)\right\rangle_\xi}{dt} = -\gamma\left\langle v(t)\right\rangle_\xi + F_0\delta(t) = -\gamma\left\langle v(t)\right\rangle_\xi + F_0\frac{d\Theta(t)}{dt}$$

$$\text{Solution: } \left\langle v(t)\right\rangle_\xi = \frac{F_0}{m}\mathrm{e}^{-\gamma t/m}\ \Theta(t) \equiv K(t)F_0$$

response function

$$K(t) = \frac{1}{m}\mathrm{e}^{-\gamma t/m}\ \Theta(t)$$

Linear response function

We can define the linear response $K(t)$ of a variable $\alpha(t)$ to an external force $F(t)$:

$$\left\langle \alpha(t)\right\rangle_F = \int_{-\infty}^{\infty} dt' K(t-t')F(t') \qquad \text{where } K(t-t') = \begin{cases} K(t-t') & \text{for } t>t' \\ 0 & \text{for } t<t' \end{cases}$$

Fourier transforms

$$\left\langle \alpha(t)\right\rangle_F = \frac{1}{2\pi}\int_{-\infty}^{\infty} d\omega \left\langle \tilde{\alpha}(\omega)\right\rangle_F \mathrm{e}^{-i\omega t} \qquad F(t) = \frac{1}{2\pi}\int_{-\infty}^{\infty} d\omega \tilde{F}(\omega)\mathrm{e}^{-i\omega t}$$

$$K(t) = \frac{\pi}{2}\int_{-\infty}^{\infty} d\omega\chi(\omega)\mathrm{e}^{-i\omega t} \qquad \chi(\omega) = \int_{-\infty}^{\infty} dtK(t)\mathrm{e}^{i\omega t}$$

$$\Rightarrow \left\langle \tilde{\alpha}(\omega)\right\rangle_F = \chi(\omega)\tilde{F}(\omega)$$

Linear response function -- simple example $K(t)=\frac{1}{m}e^{-\gamma t/m}\,\Theta(t)$

$$\chi(\omega)=\int_{-\infty}^{\infty} dt K(t) e^{i\omega t} = \frac{1}{m}\int_{-\infty}^{\infty} dt \;\; e^{-\gamma t/m} e^{i\omega t}\;\Theta(t)$$

$$=\frac{1}{\gamma - im\omega} \quad \text{for this example.}$$

Note: The pole of $\chi(z)$ has $\Im(z)<0$.

More generally: $\chi(\omega)=\chi_R(\omega)+i\chi_I(\omega)$

The real and imaginary parts of $\chi(\omega)$ satisfy the Kramers-Kronig relations:

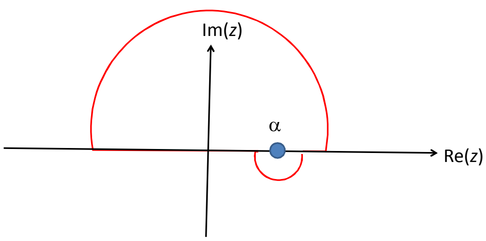
$$\chi_R(\omega)=\frac{1}{\pi}P\int_{-\infty}^{\infty} du\,\frac{\chi_I(u)}{u-\omega}$$

$$\chi_I(\omega)=-\frac{1}{\pi}P\int_{-\infty}^{\infty} du\,\frac{\chi_R(u)}{u-\omega}$$

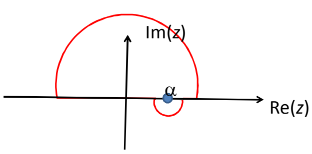
"Proof" of Kramers-Kronig relations

Consider Cauchy's integral formula for an analytic function $f(z)$:

$$\oint dz\; f(z)=0 \qquad\qquad f(\alpha)=\frac{1}{2\pi i}\oint_{\text{includes }\alpha} dz\,\frac{f(z)}{z-\alpha}$$



Kramers-Kronig transform -- continued



$$f(\alpha)=\frac{1}{2\pi i}\oint_{\text{includes }\alpha} dz\,\frac{f(z)}{z-\alpha} = \frac{1}{2\pi i}\left(\int_{-\infty}^{\infty} dz_R\,\frac{f(z_R)}{z_R-\alpha}+\underbrace{\int_{rest} dz\,\frac{f(z)}{z-\alpha}}_{=0}\right)$$

$$f(\alpha)=\frac{1}{2\pi i}\int_{-\infty}^{\infty} dz_R\,\frac{f(z_R)}{z_R-\alpha}=\frac{1}{2\pi i}P\int_{-\infty}^{\infty} dz_R\,\frac{f(z_R)}{z_R-\alpha}+\frac{1}{2}f(\alpha)$$

Kramers-Kronig transform -- continued

$$f(\alpha)= \frac{1}{2\pi i} P\int_{-\infty}^{\infty} dz_R \frac{f(z_R)}{z_R\text{-}\alpha} + \frac{1}{2} f(\alpha)$$

Suppose $f(z_R) = f_R(z_R) + i f_I(z_R)$:

$$\Rightarrow \frac{1}{2}\left(f_R(\alpha) + i f_I(\alpha)\right) = \frac{1}{2\pi i} P\int_{-\infty}^{\infty} dz_R \frac{f_R(z_R) + i f_I(z_R)}{z_R\text{-}\alpha}$$

$$\Rightarrow f_R(\alpha) = \frac{1}{\pi} P\int_{-\infty}^{\infty} dz_R \frac{f_I(z_R)}{z_R\text{-}\alpha}$$

$$f_I(\alpha) = -\frac{1}{\pi} P\int_{-\infty}^{\infty} dz_R \frac{f_R(z_R)}{z_R\text{-}\alpha}$$

Kramers-Kronig transform -- continued

$$f_R(\alpha) = \frac{1}{\pi} P\int_{-\infty}^{\infty} dz_R \frac{f_I(z_R)}{z_R\text{-}\alpha}$$

$$f_I(\alpha) = -\frac{1}{\pi} P\int_{-\infty}^{\infty} dz_R \frac{f_R(z_R)}{z_R\text{-}\alpha}$$

This Kramers-Kronig transform is useful for the susceptibility function when $f(z_R) \Rightarrow \chi(\omega)$

Must show that: 1. $f(z)$ is analytic for $z_I \geq 0$

2. $f(z)$ vanishes for $z \to \infty$

For the example: $\chi(\omega) = \dfrac{1}{\gamma - im\omega}$ requirements are met.

Fluctuation-Dissipation Theorem

Relationship of the response and correlation functions of a system near equilibrium; allows a weak external field to probe equilibrium fluctuations

Consider a function $\alpha(t)$. A force is applied:

$$F(t) = \begin{cases} 0 & t > 0 \\ F_0 & -\infty < t < 0 \end{cases}$$

Let $P(\alpha_0, F_0)$ represent the probability distribution for $\alpha(0) = \alpha_0$ in the presence of F_0.

$$\langle \alpha(t) \rangle_{F_0} = \int d\alpha_0 P(\alpha_0, F_0) \langle \alpha(t) \rangle_{\alpha_0}$$

Generally, we expect: $\langle \alpha(t) \rangle_{\alpha_0} = e^{-Mt}\alpha_0$ for $t > 0$

Fluctuation-Dissipation Theorem -- continued

$$\left\langle \alpha(t) \right\rangle_{F_0} = \int d\alpha_0 P(\alpha_0, F_0) \left\langle \alpha(t) \right\rangle_{\alpha_0}$$

$$\left\langle \alpha(t) \right\rangle_{\alpha_0} = e^{-Mt}\alpha_0 \quad \text{for } t > 0 \qquad \Rightarrow \left\langle \alpha(t) \right\rangle_{F_0} = e^{-Mt} \left\langle \alpha(0) \right\rangle_{\alpha_0}$$

Relationship to response function:

$$\left\langle \alpha(t) \right\rangle_{F} = \int_{-\infty}^{\infty} dt' K(t-t') F(t') = \frac{1}{2\pi} \int_{-\infty}^{\infty} d\omega e^{-i\omega t} \left\langle \tilde{\alpha}(\omega) \right\rangle_F$$

$$= \frac{1}{2\pi} \int_{-\infty}^{\infty} d\omega e^{-i\omega t} \chi(\omega) \tilde{F}(\omega)$$

For: $F(t) = \begin{cases} 0 & t > 0 \\ F_0 & -\infty < t < 0 \end{cases}$

$\tilde{F}(\omega) = F_0 \left(P\frac{1}{i\omega} + \pi\delta(\omega) \right)$

HW #17

Fluctuation-Dissipation Theorem -- continued

$$\tilde{F}(\omega) = F_0 \left(P\frac{1}{i\omega} + \pi\delta(\omega) \right)$$

$$\left\langle \alpha(t) \right\rangle_{F} = = \frac{1}{2\pi} \int_{-\infty}^{\infty} d\omega e^{-i\omega t} \chi(\omega) \tilde{F}(\omega)$$

$$\left\langle \alpha(t) \right\rangle_{F} = \begin{cases} \frac{F_0}{i\pi} P \int_{-\infty}^{\infty} d\omega \frac{\chi(\omega)\cos(\omega t)}{\omega} & t > 0 \\ \chi(0) F_0 & t < 0 \end{cases}$$

HW #17

Fluctuation-Dissipation Theorem -- continued

$$\left\langle \alpha(t) \right\rangle_{F_0} = \int d\alpha_0 P(\alpha_0, F_0) \left\langle \alpha(t) \right\rangle_{\alpha_0}$$

$$\left\langle \alpha(t) \right\rangle_{F_0} = e^{-Mt} \left\langle \alpha(0) \right\rangle_{\alpha_0} \quad \text{for } t > 0$$

$$\left\langle \alpha(t) \right\rangle_{F_0} = \begin{cases} \frac{F_0}{i\pi} P \int_{-\infty}^{\infty} d\omega \frac{\chi(\omega)\cos(\omega t)}{\omega} & t > 0 \\ \chi(0) F_0 & t < 0 \end{cases}$$

Note that: $\chi(0) = \frac{1}{i\pi} P \int_{-\infty}^{\infty} d\omega \frac{\chi(\omega)}{\omega}$

$$\Rightarrow e^{-Mt}\chi(0) = \frac{1}{i\pi} P \int_{-\infty}^{\infty} d\omega \frac{\chi(\omega)\cos(\omega t)}{\omega}$$

Fluctuation-Dissipation Theorem -- continued

Correlation function:

$$\langle \alpha(t)\alpha(0)\rangle = e^{-Mt}\langle \alpha_0\alpha_0\rangle$$

$$\langle \alpha(t)\alpha(0)\rangle \chi(0) = e^{-Mt}\chi(0)\langle \alpha_0\alpha_0\rangle$$

$$= \frac{1}{i\pi} P\int_{-\infty}^{\infty} d\omega \frac{\chi(\omega)\cos(\omega t)}{\omega}\langle \alpha_0\alpha_0\rangle$$

$$\Rightarrow \langle \alpha(t)\alpha(0)\rangle = \frac{1}{\chi(0)}\frac{1}{i\pi} P\int_{-\infty}^{\infty} d\omega \frac{\chi(\omega)\cos(\omega t)}{\omega}\langle \alpha_0\alpha_0\rangle$$

Note that: $\chi(0)^{-1} = T\left(\frac{\partial^2 S}{\partial \alpha^2}\right)$

$$\Rightarrow \langle \alpha(t)\alpha(0)\rangle = \frac{1}{\chi(0)}\frac{1}{i\pi} P\int_{-\infty}^{\infty} d\omega \frac{\chi(\omega)\cos(\omega t)}{\omega}\langle \alpha_0\alpha_0\rangle$$

Fluctuation-Dissipation Theorem -- example

$$\langle \alpha(t)\alpha(0)\rangle = \frac{1}{\chi(0)}\frac{1}{i\pi} P\int_{-\infty}^{\infty} d\omega \frac{\chi(\omega)\cos(\omega t)}{\omega}\langle \alpha_0\alpha_0\rangle$$

Consider a Browian particle of mass m in the presence of random noise $\xi(t)$, fluid friction γ, and an an impulse $F_0\delta(t)$:

$$m\frac{dv}{dt} = -\gamma v(t) + \xi(t) + F_0\delta(t)$$

$$m\frac{d\langle v(t)\rangle_\xi}{dt} = -\gamma\langle v(t)\rangle_\xi + F_0\delta(t) = -\gamma\langle v(t)\rangle_\xi + F_0\frac{d\Theta(t)}{dt}$$

Solution: $\langle v(t)\rangle_\xi = \frac{F_0}{m}e^{-\gamma t/m}\ \Theta(t) \equiv K(t)F_0$

$$\chi(\omega) = \int_{-\infty}^{\infty} dt K(t)e^{i\omega t} = \frac{1}{m}\int_{-\infty}^{\infty} dt\ e^{-\gamma t/m}e^{i\omega t}\ \Theta(t)$$

$$= \frac{1}{\gamma - im\omega}$$ for this example.

Fluctuation-Dissipation Theorem -- example

$$\langle \alpha(t)\alpha(0)\rangle = \frac{1}{\chi(0)}\frac{1}{i\pi} P\int_{-\infty}^{\infty} d\omega \frac{\chi(\omega)\cos(\omega t)}{\omega}\langle \alpha_0\alpha_0\rangle$$

$$\chi(\omega) = \frac{1}{\gamma - im\omega}$$

$$\langle \alpha_0\alpha_0\rangle = \langle v_0^2\rangle = \frac{kT}{m}$$

$$\langle \alpha(t)\alpha(0)\rangle \equiv \langle v(t)v(0)\rangle = \frac{\gamma kT}{m}\frac{1}{i\pi} P\int_{-\infty}^{\infty} d\omega \frac{\chi(\omega)\cos(\omega t)}{\omega}$$

$$= \frac{kT}{m}e^{-\gamma t/m}$$

Microscopic linear response theory

Consider a Hamiltonian consisting of H_0 representing the system in absence of a field and a small perturbing field described by ΔH :

$$H(t) = H_0(t) + \Delta H(t)$$

In terms of the density operator:

$$i\hbar \frac{\partial \rho(t)}{\partial t} = \left[H(t), \rho(t) \right]$$

Assume: $\rho(t) = \rho_{eq}(t) + \Delta\rho(t)$ where $\rho_{eq}(t) = \frac{e^{-\beta H_o}}{\mathrm{Tr}\left(e^{-\beta H_o}\right)}$

$$i\hbar \frac{\partial \rho(t)}{\partial t} = \left[\Delta H(t), \rho_{eq}(t) \right] + \left[H_0(t), \Delta\rho(t) \right] + \left[\Delta H(t), \Delta\rho(t) \right]$$

(→ 0)

Microscopic linear response theory -- continued

$$i\hbar \frac{\partial \rho(t)}{\partial t} \approx \left[\Delta H(t), \rho_{eq}(t) \right] + \left[H_0(t), \Delta\rho(t) \right]$$

Assume $\Delta\rho(t \to -\infty) = 0$

$$\Delta\rho(t) \approx \frac{1}{i\hbar} \int_{-\infty}^{t} dt' \left[e^{iH_0(t-t')/\hbar} \Delta H(t) e^{-iH_0(t-t')/\hbar}, \rho_{eq}(t) \right]$$