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

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Course Webpage: http://www.wfu.edu/~natalie/s14phy770

Lecture 23

Review and perspective

- **Comments about some homework problems**
- **Treatment of multicomponent systems**

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

	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	Chap. 9	Transport theory (class 12-1:45 PM)	#18	04/10/2014
20	Tue: 04/08/2014	Chap. 9	The Boltzmann Equation (class 12-1:45 PM)	#19	04/10/2014
21	Thur: 04/10/2014	Chap. 9	The Boltzmann Equation (class 12-1:45 PM)	#20	04/17/2014
22	Tue: 04/15/2014	Chap. 9	The Bolzmann Equation (class 12-1:45 PM)	#21	04/17/2014
23	Thur: 04/17/2014		Review and highlights (class 12-1:45 PM)		
24	Tue: 04/22/2014		Review and highlights (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)		

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Comments about homework problems:

PHY 770 -- Assignment #16

March 27, 2014

Continue reading Chapter 7 in **Reichl**.

1. Solve problem 7.2 in the 3rd edition text

Note: This is the similar to problem is S5.6 in the 2nd edition text.

HW #16 -- continued

7.2 A Brownian particle of mass *m* is attached to a harmonic spring with force constant *k*, and is driven by an external force *F(t)*. The particle is constrained to move in one dimension. The Langevin equation is

$$m\frac{d^2x(t)}{dt^2}+\gamma\frac{dx(t)}{dt}+m\omega_0^2x(t)=\xi(t)+F(t)$$

(a) Find the equilibrium correlation function $\langle x(t)x(0)\rangle_{T\xi}$ directly from the solution of the Langevin equation assuming that $\langle \xi(t)\rangle_{\xi}=0$ and $\langle x(0)x(0)\rangle_T=kT/(m\omega_0^2)$, $\langle x(0)v(0)\rangle_T=0$, etc.

(b) Find the equilibrium correlation function $\langle x(t)x(0)\rangle_{T\xi}$ from the fluctuation-dissipation theorem relation

$$\langle x(t)x(0)\rangle_T=kT\frac{1}{i\pi}\int_{-\infty}^{\infty}d\omega\frac{\chi(\omega)\cos(\omega t)}{\omega}$$

where for this case: $\chi(\omega)=\dfrac{-1/m}{\omega^2+i\frac{\gamma}{m}\omega-\omega_0^2}$

HW #16 -- continued

First consider solutions to homogeneous equation:

$$m\frac{d^2x(t)}{dt^2}+\gamma\frac{dx(t)}{dt}+m\omega_0^2x(t)=0$$

$$x(t)=Ae^{-\frac{\gamma}{2m}t-\sqrt{\left(\frac{\gamma}{2m}\right)^2-\omega_0^2}\,t}+Be^{-\frac{\gamma}{2m}t+\sqrt{\left(\frac{\gamma}{2m}\right)^2-\omega_0^2}\,t}$$

Note: we are assuming the over-damped case

Imposing boundary conditions:

$x(0)\equiv x_0$ and $\frac{dx(0)}{dt}\equiv v_0$:

$$x(t)=e^{-\frac{\gamma}{2m}t}\left(x_0\cosh\left(\sqrt{\left(\frac{\gamma}{2m}\right)^2-\omega_0^2}\,t\right)+\frac{v_0+\frac{\gamma}{2m}x_0}{\sqrt{\left(\frac{\gamma}{2m}\right)^2-\omega_0^2}}\sinh\left(\sqrt{\left(\frac{\gamma}{2m}\right)^2-\omega_0^2}\,t\right)\right)$$

We can argue that since the random force averages to 0, the correlation function depends only on the homogeneous solution.

HW #16 -- continued

$$x(t)=e^{-\frac{\gamma}{2m}t}\left(x_0\cosh\left(\sqrt{\left(\frac{\gamma}{2m}\right)^2-\omega_0^2}\,t\right)+\frac{\left(v_0+\frac{\gamma}{2m}x_0\right)e^{-\frac{\gamma}{2m}t}}{\sqrt{\left(\frac{\gamma}{2m}\right)^2-\omega_0^2}}\sinh\left(\sqrt{\left(\frac{\gamma}{2m}\right)^2-\omega_0^2}\,t\right)\right)$$

The initial values x_0 and v_0 can be treated as random variables with

$\langle x_0^2\rangle_T=\frac{kT}{m\omega_0^2}$ and $\langle x_0v_0\rangle_T=0$.

$$\langle x(t)x(0)\rangle_T=$$

$$\langle x_0^2\rangle_T\,e^{-\frac{\gamma}{2m}t}\left(\cosh\left(\sqrt{\left(\frac{\gamma}{2m}\right)^2-\omega_0^2}\,t\right)+\frac{\frac{\gamma}{2m}}{\sqrt{\left(\frac{\gamma}{2m}\right)^2-\omega_0^2}}\sinh\left(\sqrt{\left(\frac{\gamma}{2m}\right)^2-\omega_0^2}\,t\right)\right)$$

HW #16 -- continued

Now consider that dissipation-fluctuation formulation:

$$\left\langle x(t)x(0)\right\rangle_T = kT\frac{1}{i\pi}\int_{-\infty}^{\infty}d\omega\frac{\chi(\omega)\cos(\omega t)}{\omega}$$

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

with: $\chi(\omega) = \dfrac{-1/m}{\omega^2 + i\frac{\gamma}{m}\omega - \omega_0^2}$

We will need to contour integration methods to evaluate the integrals:

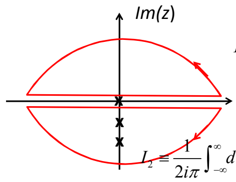
$$I_1 \equiv \frac{1}{2i\pi}\int_{-\infty}^{\infty}d\omega\frac{\chi(\omega)}{\omega}e^{i\omega t} \qquad I_2 \equiv \frac{1}{2i\pi}\int_{-\infty}^{\infty}d\omega\frac{\chi(\omega)}{\omega}e^{-i\omega t}$$

Note that the denominator of the integrals $\omega(\omega^2 + i\frac{\gamma\omega}{m} - \omega_0^2)$:

has poles at the values $\omega_P = 0, ir_+, ir_-$

where $r_\pm \equiv -\frac{\gamma}{2m} \pm \sqrt{\left(\frac{\gamma}{2m}\right)^2 - \omega_0^2}$

HW #16 -- continued



$$I_1 \equiv \frac{1}{2i\pi}\int_{-\infty}^{\infty}d\omega\frac{\chi(\omega)}{\omega}e^{i\omega t} = 0$$

$$I_2 \equiv \frac{1}{2i\pi}\int_{-\infty}^{\infty}d\omega\frac{\chi(\omega)}{\omega}e^{-i\omega t} = \left(\text{Res}\left(\omega = ir_-\right) + \text{Res}\left(\omega = ir_+\right)\right)$$

$$\left\langle x(t)x(0)\right\rangle_T =$$

$$\frac{kT}{m\omega_0^2}e^{-\frac{\gamma}{2m}t}\left(\cosh\left(\sqrt{\left(\frac{\gamma}{2m}\right)^2 - \omega_0^2}\,t\right) + \frac{\frac{\gamma}{2m}}{\sqrt{\left(\frac{\gamma}{2m}\right)^2 - \omega_0^2}}\sinh\left(\sqrt{\left(\frac{\gamma}{2m}\right)^2 - \omega_0^2}\,t\right)\right)$$

Comments about homework problems:

PHY 770 -- Assignment #18

April 3, 2014

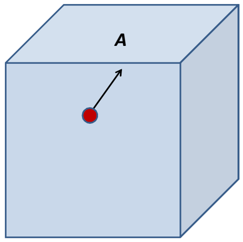
Start reading Chapter 9 in **Reichl**.

1. Work problem #9.1 in the 3rd edition of **Reichl**.

Note: This is equivalent to problem #11.1 in the in the 2nd edition text.

A dilute gas of density *n* is contained in a cubic box and is in equilibrium with the walls at temperature*T*. Find the number of particles per unit area per unit time which collide with the walls and have magnitude of velocity greater than v_0.

HW #18 -- continued



Maxwell Boltzmann distribution:

$$f(\mathbf{p}) = n\left(\frac{\beta}{2\pi m}\right)^{3/2} e^{-\beta p^2/(2m)}$$

Probability per unit time that particle will hit top face with velocity magnitude greater than v_0 :

$$P = \int_{\frac{p}{m}>v_0} d^3p \frac{p_z \Theta(p_z)}{m} f(\mathbf{p})$$

Treatment of multicomponent systems including chemical reactions (Sect. 3.10 of 3rd Ed. Reichl)

Summary of thermodynamic potentials (note $X \rightarrow V$, $Y \rightarrow -P$)

Potential	Variables	Total Diff	Fund. Eq.
U	***S,X,N$_i$***	$dU = TdS + YdX + \sum_i \mu_i dN_i$	$U = TS + YX + \sum_i \mu_i N_i$
H	***S,Y,N$_i$***	$dH = TdS - XdY + \sum_i \mu_i dN_i$	$H = U - YX$
A	***T,X,N$_i$***	$dA = -SdT + YdX + \sum_i \mu_i dN_i$	$A = U - TS$
G	***T,Y,N$_i$***	$dG = -SdT - XdY + \sum_i \mu_i dN_i$	$G = U - TS - YX$
Ω	***T,X,μ$_i$***	$d\Omega = -SdT + YdX - \sum_i \mu_i dN_i$	$\Omega = U - TS - \sum_i \mu_i N_i$

Derivative relationships of thermodynamic potentials

Internal energy $U(S, X, \{N_i\})$:

$$T = \left(\frac{\partial U}{\partial S}\right)_{X,\{N_i\}} \quad Y = \left(\frac{\partial U}{\partial X}\right)_{S,\{N_i\}} \quad \mu_i = \left(\frac{\partial U}{\partial N_i}\right)_{S,X,\{N_j\}}$$

Enthalpy $H(S, Y, \{N_i\})$:

$$T = \left(\frac{\partial H}{\partial S}\right)_{Y,\{N_i\}} \quad X = \left(\frac{\partial H}{\partial Y}\right)_{S,\{N_i\}} \quad \mu_i = \left(\frac{\partial H}{\partial N_i}\right)_{S,Y,\{N_j\}}$$

Helmholz free energy $A(T, X, \{N_i\})$:

$$S = -\left(\frac{\partial A}{\partial T}\right)_{X,\{N_i\}} \quad Y = \left(\frac{\partial A}{\partial X}\right)_{T,\{N_i\}} \quad \mu_i = \left(\frac{\partial A}{\partial N_i}\right)_{T,X,\{N_j\}}$$

Gibb's free energy $G(T, Y, \{N_i\})$:

$$S = -\left(\frac{\partial G}{\partial T}\right)_{Y,\{N_i\}} \quad X = -\left(\frac{\partial G}{\partial Y}\right)_{T,\{N_i\}} \quad \mu_i = \left(\frac{\partial G}{\partial N_i}\right)_{T,Y,\{N_j\}}$$

Properties of the Gibb's free energy

$$U = TS - PV + \sum_i \mu_i N_i$$

$$G = U - TS + PV = \sum_i \mu_i N_i$$

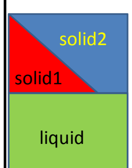
Further analysis from Gibb's free energy $G(T, P, \{N_i\})$:

$$S = -\left(\frac{\partial G}{\partial T}\right)_{P,\{N_i\}} \quad V = \left(\frac{\partial G}{\partial P}\right)_{T,\{N_i\}} \quad \mu_i = \left(\frac{\partial G}{\partial N_i}\right)_{T,P,\{N_j\}}$$

$$\Rightarrow S = -\sum_i \left(\frac{\partial \mu_i}{dT}\right)_{P,\{N_j\}} N_i \quad V = \sum_i \left(\frac{\partial \mu_i}{dP}\right)_{T,\{N_j\}} N_i$$

Properties of the Gibb's free energy -- Gibbs phase rule and phase equilibria

Consider a system at uniform temperature *T* and pressure *P* with *n* chemical constituents. How many distinct phases *r* of this system can exist in equilibrium?



Enumeration of all of possible components and phases:

$N_i = \sum_{j=1}^{r} \bar{N}_{i,j}$ where $\bar{N}_{i,j} \equiv$ number of component i in phase j

Generalization of Gibbs free energy:

$G = \sum_{i,j} \bar{\mu}_{i,j} \bar{N}_{i,j}$

At equilibrium: $\bar{\mu}_{i,1} = \bar{\mu}_{i,2} \ldots \bar{\mu}_{i,r}$

Accounting -- # independent variables: $2 + r(n-1)$

independent constraints: $n(r-1)$

degrees of freedom: $f = 2 + r(n-1) - n(r-1)$

$f = 2 + n - r$

Properties of the Gibb's free energy -- Gibbs phase rule and phase equilibria -- continued

degrees of freedom: $f = 2 + n - r$

Examples

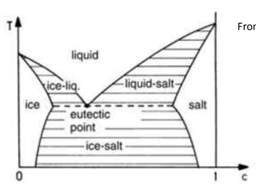
$\Rightarrow n = 1$:

for $r = 1, f = 2$ T, P free to vary

for $r = 2, f = 1$ $P = P(T)$ on phase boundary curve

for $r = 3, f = 0$ can occur at special (P, T) 'triple point'

$\Rightarrow n = 2$: such as water and amonium cloride at concentration c



From Schwabl, Statistical Mechanics

Fig. 3.38. The phase diagram of a mixture of sal ammoniac (ammonium chloride) and water. In the horizontally shaded regions, ice and liquid, liquid and solid salt, and finally ice and solid salt coexist with each other.

Properties of the Gibb's free energy -- multicomponent ideal gas

$$G = \sum_i \mu_i N_i$$

For example, consider a reaction at fixed T and P:

$$2\mathrm{H_2} + \mathrm{O_2} \leftrightarrow 2\mathrm{H_2O}$$

$$-2\mathrm{H_2O} + 2\mathrm{H_2} + \mathrm{O_2} = 0 \quad \text{General notation: } \sum_{i=1}^{n} \nu_i A_i = 0$$

Change in Gibbs free energy with fixed T and P:

$$dG = \sum_{i=1}^{n} \mu_i dN_i = 0 \quad \text{at equilibrium}$$

Because of the relationships between the components

it follows that $\sum_{i=1}^{n} \mu_i \nu_i = 0$

Multicomponent ideal gas and possible chemical reactions -- continued

Change in Gibbs free energy with fixed T and P:

$$\sum_{i=1}^{n} \mu_i (T,P) \nu_i = 0$$

Estimation of the chemical potentials:

- For each i, assume independent ideal gas particles with internal energies determined by electronic, internal and kinetic energies
- Kinetic energy contributions expressed in terms of thermal wavelength

$$\lambda_i = \left(\frac{\hbar^2}{2\pi m_i kT} \right)^{1/2}$$

- Canonical partition function: $Z = \prod_{i=1}^{n} Z_i$
- For each species i: $-kT \ln(Z_i) \approx N_i \left(\varepsilon_i^{el} + \varepsilon_i^{\text{int}} - kT \left(1 + \ln \frac{V}{N_i \lambda_i^3} \right) \right)$

Multicomponent ideal gas and possible chemical reactions -- continued

Helmholz free energy for this system

$$A = -kT \ln Z \approx \sum_{i=1}^{n} N_i \left(\varepsilon_i^{el} + \varepsilon_i^{\text{int}} - kT \left(1 + \ln \frac{V}{N_i \lambda_i^3} \right) \right)$$

$$\mu_i = \left(\frac{\partial A}{\partial N_i} \right)_{T,V,\{N_j\}} = \varepsilon_i^{el} + \varepsilon_i^{\text{int}} - kT \ln \frac{V}{N_i \lambda_i^3}$$

For an ideal gas: $PV = NkT$ where $\sum_{i=1}^{n} N_i = N$

Let $c_i \equiv \frac{N_i}{N}$ $\quad \mu_i(T,P,c_i) = \varepsilon_i^{el} + \varepsilon_i^{\text{int}} - kT \ln \left(\frac{kT/P}{c_i \lambda_i^3} \right)$

$$\Rightarrow \mu_i(T,P,c_i) = \mu_i^0(T) + kT \ln(c_i P)$$

Multicomponent ideal gas and possible chemical reactions -- continued

Recall: $\sum_{i=1}^{n} \mu_i \nu_i = 0$

$$\mu_i(T,P,c_i) = \mu_i^0(T) + kT\ln(c_i P)$$

$$\sum_{i=1}^{n}\left(\mu_i^0(T) + kT\ln(c_i P)\right)\nu_i = 0$$

$$\sum_{i=1}^{n}\left(\frac{\nu_i \mu_i^0(T)}{kT} + \nu_i \ln(c_i P)\right) = 0$$

Define: $\ln(K(T,P)) \equiv -\sum_{i=1}^{n}\left(\frac{\nu_i \mu_i^0(T)}{kT} + \nu_i \ln(P)\right)$

$$\Rightarrow \sum_{i=1}^{n}\ln\left(c_i^{\nu_i}\right) = \ln\left(\prod_{i=1}^{n}\left(c_i^{\nu_i}\right)\right) = \ln(K(T,P))$$

$$\Rightarrow \prod_{i=1}^{n}\left(c_i^{\nu_i}\right) = K(T,P)$$

Multicomponent ideal gas and possible chemical reactions -- continued

$$\prod_{i=1}^{n}\left(c_i^{\nu_i}\right) = K(T,P)$$

Example:

$-2H_2O+2H_2+O_2 = 0$ General notation: $\sum_{i=1}^{n} \nu_i A_i = 0$

$$\prod_{i=1}^{n}\left(c_i^{\nu_i}\right) = \frac{[H_2]^2[O_2]}{[H_2O]^2} = K(T,P)$$

Multicomponent ideal gas and possible chemical reactions -- continued

$$\prod_{i=1}^{n}\left(c_i^{\nu_i}\right) = \frac{[H_2]^2[O_2]}{[H_2O]^2} = K(T,P)$$

$2H_2 + O_2 \leftrightarrow 2H_2O$

Suppose $[H_2O] = 1 - x$

$[H_2] = x$

$[O_2] = x/2$

$$\frac{x^3}{2(1-x)^2} = K(T,P)$$