

Chemistry 553, Thermodynamics

Final exam

Due: noon on Thursday 17 March 2011 in room 104 Gilbert

Rules: books/notes ... OK; human resources ...not OK

- 10
1. Basic thermodynamics. Water freezes at $T_f^0 = 273K$ at 1 bar. The entropy for this process is given by the ratio of the heat of fusion to the absolute temperature. Supercooled water freezes at a temperature slightly below T_f^0 . Derive $\Delta S_{fusion}(T < T_f^0)$, first using a power series expansion in T and compare your result with that obtained by replacing the process of irreversible freezing by a set of reversible steps.

2. Partition functions in the canonical ensemble. Suppose that the single particle partition function is

15

$$q_T(N, V, T) = \frac{(V - Nb)e^{\beta \rho a}}{\Lambda^3} \quad (1)$$

where a, b are constants. What is the equation of state, the entropy and the critical exponent δ for this fluid, where

$$P - P_c \simeq (\rho - \rho_c)^\delta \quad \text{along } T = T_c \quad (2)$$

3. Ideal gas chemical equilibrium. Derive the T -dependence of the equilibrium constant for the gas phase dimerization of water in the temperature range $\Theta_R \ll T \ll \Theta_v$. Write the result in the form

5

$$K_d(T) \simeq T^a e^{-b/T} \quad (3)$$

Identify the values or functions described by a, b .

4. Ad hoc non-ideal fluids. Hildebrand's theory of non-ideal liquid mixtures predicts that the Helmholtz energy obeys:

$$\frac{A(N_1, N_2, T)}{Nk_B} = T[x_1 \ln(x_1) + x_2 \ln(x_2)] + u_1 x_1 + u_2 x_2 + u_{12} x_1 x_2 \quad (4)$$

15

a) Derive the Henry's law constant, use the chemical potential route. b) Calculate ΔA_{mixing} . c) Plot ΔA_{mixing} for the two component fluid and locate the mole fractions of the coexisting phases. Select parameters that give rise to two-phase equilibria and a critical point.

5. Exact statistical mechanics. Using the definition of $g(r)$,

10

$$\frac{g(r_1, r_2)}{V^2} = \frac{\int dr_3 \cdots dr_n e^{-\beta U}}{\int dr_1 dr_2 \cdots dr_N e^{-\beta U}} \quad (5)$$

derive the expression for the energy for a fluid of rigid, spherical top molecules, viz.,

$$\frac{E}{Nk_B T} = 3 + \frac{\rho}{2k_B T} \int u(r)g(r)dr \quad (6)$$

Start your derivation with

$$A = -k_B T \ln Q_N(V, T), \quad Q_N(V, T) = \frac{1}{N! h^{3N}} \int dr_1 dr_2 \cdots dr_n dp_1 \cdots dp_N dL_1 \cdots dL_N e^{-\beta(T+U)} \quad (7)$$

The kinetic energy has translational and rotational parts (both to be treated classically) and the potential energy is pairwise additive. L_i is the angular momentum of the i 'th particle.

6. Phase transitions and order parameters. The Helmholtz energy for an N particle fluid comprised of hard rods is given by the Landau expansion

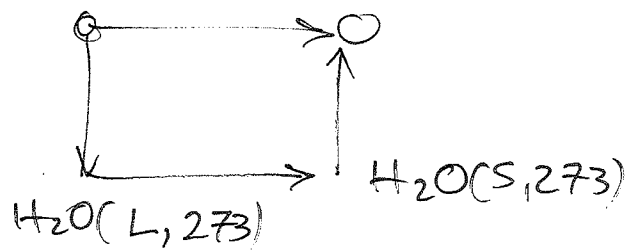
$$\frac{A(S)}{Nk_B T} \simeq \frac{A(0)}{Nk_B T} + 2S^2(1 - a\rho^*) - S^3 + 4S^4 \quad (8)$$

where S is the alignment order parameter, $S = \langle P_2(\cos \theta) \rangle$. Here a is a measure of the shape anisotropy of the rod, $a \simeq (L_{long} - L_{short})^2 / L_{short}^2$, where L is the length along a long or short axis.

Find the lowest density at which an aligned phase can form and the non-zero order parameter for the nematic phase at the transition. We claim this transition is first order. What tells us that?

Exam 2

1. Irreversible freezing



so

$$\Delta S(L \rightarrow S, 263) = \int_{263}^{273} C_p(L) \frac{dT}{T} + \Delta S(L \rightarrow S, 273) + \int_{273}^{263} C_p(S) \frac{dT}{T}$$

$$\Delta S(L \rightarrow S, 263) = (T_{263} - T_{273}) \frac{C_p(S) - C_p(L)}{T} + \Delta S(L \rightarrow S, 273)$$

By the power series method, we say

$$\Delta S(L \rightarrow S, 263) = \Delta S(L \rightarrow S, 273)$$

$$+ \left[\frac{\partial \Delta S(L \rightarrow S)}{\partial T} \right]_{T=273} \Delta T, \quad \Delta T = T - 273$$

$$\underbrace{\frac{\Delta C_p}{T} = \frac{C_p(S) - C_p(L)}{T}}_{T=273}$$

\therefore to first order, both approaches are equivalent.

$$2. \quad A = -k_B T \ln Q_N$$

$$Q_N = \frac{q^N}{N!} = \frac{1}{N!} \frac{(V - Nb)^N}{\Delta^{3N}} \exp(a\beta N\beta)$$

$$a\beta N\beta = a \cdot \frac{N}{V} \cdot N\beta = a\beta N^2/V$$

$$P = -\left(\frac{\partial A}{\partial V}\right)_T = k_B T \left(\frac{\partial \ln Q_N}{\partial V}\right)_{T, N}$$

$$S = -\left(\frac{\partial A}{\partial T}\right)_{V, N} = k_B \frac{\partial}{\partial T} \left\{ T \ln Q \right\}_{N, V}$$

As for the pressure,

$$\frac{\partial \ln Q}{\partial V} = \frac{\partial}{\partial V} \left\{ \ln (V - Nb)^N + a\beta N^2/V \right\}$$

$$= \frac{N}{V - Nb} - a\beta \frac{N^2}{V^2}$$

$$P = k_B T \left\{ \frac{N}{V - Nb} - a\beta \frac{N^2}{V^2} \right\}$$

$$P = \frac{k_B T \rho}{1 - b\rho} - a\rho^2 \quad \equiv \text{van der Waals}$$

As for the entropy

$$S = k_B \ln Q + k_B T \frac{\partial \ln Q}{\partial T}$$

$$\text{cet. } \left(\frac{\partial \ln Q}{\partial T}\right) = \frac{\partial}{\partial T} a\beta N^2/V = \frac{-a}{k_B T^2} N^2/V$$

$$S = k_B \ln Q - a\rho N/T$$

$$\ln Q = N \ln q - \ln N! = N \ln(qe/N)$$

so that

$$\ln Q = N \ln \left(\frac{(V-Nb)e^{a\rho/k_B T}}{\Delta^3} \right)$$

$$\frac{\partial \ln Q}{\partial T} = N \frac{\partial}{\partial T} \left\{ \frac{a\rho}{k_B T} - 3 \ln \Delta \right\}$$

$$\Delta = h / (2\pi m k_B T)^{1/2}$$

$$\frac{\partial \ln Q}{\partial T} = N \left\{ \frac{-a\rho}{k_B T^2} + \frac{3}{2} \frac{1}{T} \right\}$$

assemble the parts

$$S = N k_B \ln(qe/N) + N k_B \left(-\frac{a\rho}{k_B T} + \frac{3}{2} \right)$$

$$S = N k_B \ln \left(\underbrace{qe^{-a\rho/k_B T}}_{\uparrow} e^{5/2} / N \right)$$

interesting since

$$q \exp(-a\rho/k_B T) = \frac{(V-Nb)}{\Delta^3}$$

The critical exponent, δ , arises from the power series

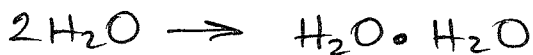
$$P = P_c + \left(\frac{\partial P}{\partial p}\right)_{T_c} (p - p_c) + \frac{1}{2} \left(\frac{\partial^2 P}{\partial p^2}\right)_{T_c} (p - p_c)^2 + \frac{1}{3!} \left(\frac{\partial^3 P}{\partial p^3}\right)_c (p - p_c)^3$$

vanishes by fiat.

$$p - p_c \sim \frac{(\Delta p)^3}{3!} \left(\frac{\partial^3 P}{\partial p^3}\right)_c \quad \text{and } \delta = 3$$

for any eq. of state.

3.



$$K_d(T) = \frac{(Q_{\text{dimer}}/V)}{(Q_{\text{mono}}/V)^2} = \frac{T^{3/2} T^{3/2} e^{\beta D_0(\text{dimer})}}{(T^{3/2} T^{3/2} e^{\beta D_0(\text{mono})})^2}$$

$$K_d(T) \sim \frac{1}{T^3} \exp(\beta [D_0(\text{dimer}) - 2D_0(\text{mono})])$$

$$a = -3, \quad b/T = \text{---}$$

$$\frac{\Delta A_{\text{MIX}}}{NR_{\text{BT}}} = x_1 \ln x_1 + x_2 \ln x_2 + \left(\frac{U_{12}}{T}\right) x_1 x_2$$

$$\frac{\partial \Delta A_{\text{MIX}}}{\partial x} = 0 \Rightarrow \overset{\text{use}}{\frac{\partial x_2}{\partial x_1}} = -1$$

$$\begin{aligned} \frac{\partial \Delta A_{\text{MIX}}}{\partial x_1} &= \ln x_1 + 1 - [\ln x_2 + 1] + \frac{U_{12}}{T} [x_2 - x_1] \\ &= \ln(x_1/x_2) + \frac{U_{12}}{T} (x_2 - x_1) = 0 \end{aligned}$$

$$\frac{\partial^2 \Delta A_{\text{MIX}}}{\partial x_1^2} = \frac{1}{x_1} + \frac{1}{x_2} - \frac{2U_{12}}{T} = 0 \Rightarrow \frac{U_{12}}{T} = 2$$

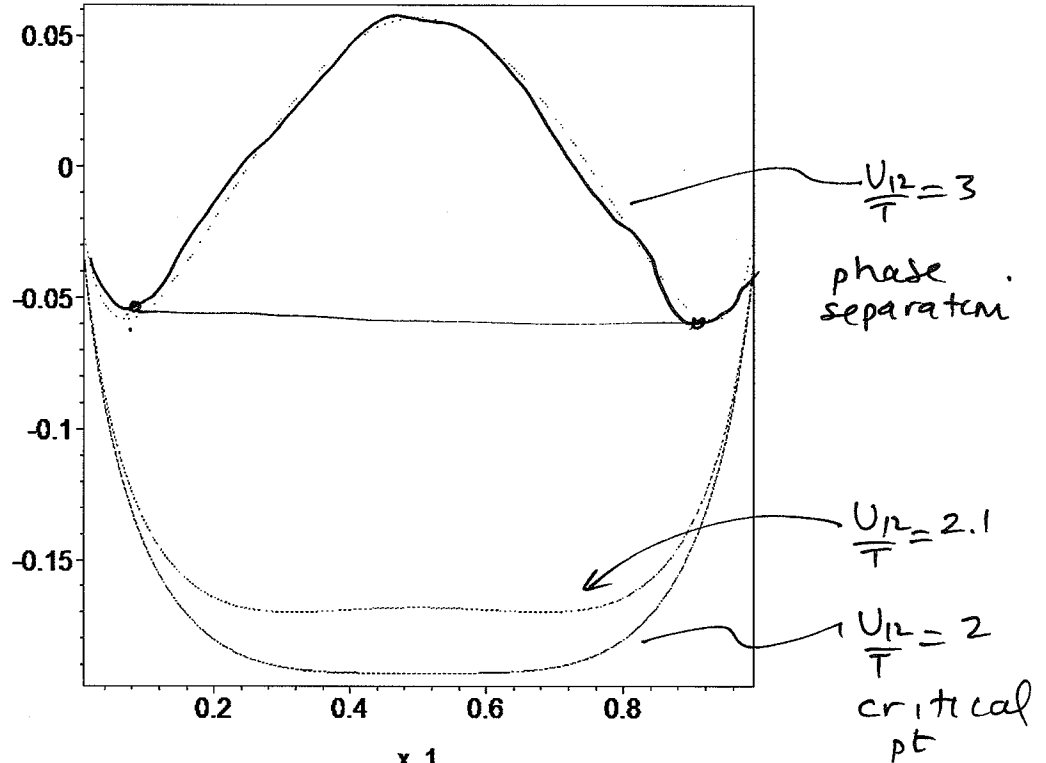
is the critical point.

see graph.

```

> x_2 := 1 - x_1; A_mix := x_1*ln(x_1) + x_2*ln(x_2) + uT*x_1*x_2;
      x_2 := 1 - x_1
      A_mix := x_1 ln(x_1) + (1 - x_1) ln(1 - x_1) + uT x_1 (1 - x_1)
> plot([subs(uT=2,A_mix),subs(uT=2.1,A_mix),subs(uT=3,A_mix)],x_1=0.01..0.99,axes=boxed);

```



```

> solve(diff(diff(A_mix,x_1),x_1)=0,x_1);

```

$$\frac{uT + \sqrt{uT^2 - 2uT}}{2uT}, \frac{uT - \sqrt{uT^2 - 2uT}}{2uT}$$

$(U_{12}/T) > 2U_{11}/T$
 $\text{or } U_{12}/T \geq 2 \text{ c.p.}$

$$4. \quad \mu_1 = \left(\frac{\partial A}{\partial N_1} \right)_{N_2, V, T}$$

$$A = k_B T \left\{ N_1 \ln \frac{N_1}{N_1 + N_2} + N_2 \ln \frac{N_2}{N_1 + N_2} \right\} \\ + N_1 k_B U_1 + N_2 k_B U_2 + \frac{N_1 N_2}{N_1 + N_2} k_B U_{12}$$

$$\left(\frac{\partial A}{\partial N_1} \right)_{N_2, V, T} = k_B T \left\{ \ln x_1 + 1 - \frac{N_1}{N_1 + N_2} - \frac{N_2}{N_1 + N_2} \right\} \\ + k_B U_1 + \underbrace{\left[x_2 + \frac{N_1 N_2}{(N_1 + N_2)^2} (-1) \right]}_{x_2^2} U_{12} k_B$$

so that

$$\beta \mu_1 = \ln x_1 + U_1/T + U_{12} x_2^2 / T \\ = \ln (x_1 \exp(U_1/T) \exp(U_{12} x_2^2 / T)) \\ \Rightarrow \\ p = p_1^0 x_1 \exp(U_{12} x_2^2 / T)$$

Henry's law \Rightarrow

$$a) \quad K_H = p_1^0 \exp(+U_{12} x_2^2 / T)$$

$$b) \quad \Delta A_{\text{mixing}} = A(N_1, N_2, T) - x_1 A(N_1, 0, T) \\ - x_2 A(N_2, N_1=0, T) \\ = N k_B T \{ x_1 \ln x_1 + x_2 \ln x_2 \} + N k_B U_{12} x_1 x_2$$

$$5. Q_N(T, V) = \frac{1}{N!} \frac{1}{h^{6N}} \int dr_1 \dots dr_N dp_1 \dots dp_N dL_1 \dots dL_N e^{-\beta H}$$

First consider the momentum integrals

$$\underbrace{\int \tilde{dp}_i \exp(-\beta p_i^2 / 2m)}_{(2\pi m k_B T)^{3/2}} \underbrace{\int \tilde{dL}_i \exp(-\beta L_i^2 / 2I)}_{(2\pi I k_B T)^{3/2}}$$

$$\text{so } Q_N = \frac{\left[\left(\frac{2\pi m k_B T}{h^2} \right)^{3/2} \left(\frac{2\pi I k_B T}{h^2} \right)^{3/2} \right]^N}{N!} Z_N$$

$$\text{with } Z_N = \int dr_1 \dots dr_N \exp(-\beta U)$$

$$\text{Recall, } d(A/T) = (1/T)dA - (A/T^2)dT = -\frac{SdT}{T} - \frac{A dT}{T^2}$$

$$d(A/T)_{\checkmark} = -E/T^2, \quad A = -k_B T \ln Q$$

$$\frac{d}{dT} k_B \ln Q = E/T^2, \quad E = k_B T^2 \frac{\partial}{\partial T} \ln Q$$

$$\ln Q = \ln T^{3N} + \ln Z_N \quad \text{and now}$$

$$E = 3N k_B T + k_B T^2 \frac{\partial}{\partial T} \ln Z_N$$

$$\frac{d}{dT} \ln Z_N = \frac{1}{Z_N} \int d1 \dots dN \left(+ \frac{U}{k_B T^2} \right) e^{-\beta U}$$

$$= + \frac{1}{Z_N} \frac{N \cdot (N-1)}{2 k_B T^2} \frac{\int d1 d2 \dots dN U_{12} e^{-\beta U}}{\int d1 \dots dN e^{-\beta U}}$$

$$\equiv g(r_{12}) / v^2$$

so

$$\begin{aligned} (d/dT) \ln Z_N &= + \frac{\rho^2}{2 k_B T^2} \int d1 d2 U(r_{12}) g(r_{12}) \\ &= + \frac{\rho^2 v}{2 k_B T^2} \int dr U(r) g(r) \end{aligned}$$

and

$$E = 3N k_B T + \frac{N \rho}{2} \int dr U(r) g(r)$$

$$\Rightarrow N k_B T \left[3 + \frac{\beta \rho}{2} \int dr U(r) g(r) \right]$$

6. Liquid crystals

$$\frac{A(s)}{NRBT} = \frac{A(0)}{NRBT} + 2s^2(1 - ap^*) - s^3 + 4s^4$$

$$\left(\frac{\partial A(s)}{\partial s}\right) = 0 = 4s(1 - ap) - 3s^2 + 16s^3$$

$$\text{or } 16s^2 - 3s + 4(1 - ap) = 0$$

roots:

$$s = \frac{+3 \pm \left[9 - 4 \cdot 16 \cdot 4(1 - ap)\right]^{1/2}}{32}$$

$$= 3 \pm \frac{\left[256 ap^* - 247\right]^{1/2}}{32}$$

when $256 ap^* \geq 247$ s switches
from 0 to $3/32$

$$\therefore ap^* = \frac{247}{256}$$

First order because change discontinuous
at $ap^* = 247/256$, and $a > 0$.