Problem Set PS10

ISSUED: 3/30/99 **Due: 4/11/00 (Tuesday)**

Prof. Darin J. Ulness Name ______________________

Instructions. Complete all questions before class on the due date. You are encouraged to work together. Be sure to struggle with the problem before seeking help. Many of the exercises are very similar to problems in the book. Understanding the solution to these problems will be helpful in completing the assigned exercises.

Mathematical Exercises

1. How does $\frac{x-\bar{x}}{\bar{x}}$ compare with $\frac{x-\bar{x}}{x}$ as $x \rightarrow \bar{x}$, where $\bar{x}$ is a constant. (Hint: subtract one from the other and take the limit as $x \rightarrow \bar{x}$).

2. Identify the exponent of x which dominates the behavior of

   (a)

$$\lim_{x \rightarrow 0} \frac{x^3}{(x^3 + x^2 + x + 1)}$$

   (b)

$$\lim_{x \rightarrow 0} x^3 \left(x^3 + x^2 + x + 1\right)$$

Exercises

3. If the normalized variable for volume is $v = \frac{V - V_c}{V_c}$, show that the unintiutive result $v \approx -\bar{\varrho}$ is true near the critical point (you might naively expect $v \approx 1/\bar{\varrho}$). Note the above relation is not exactly true (hence the $\approx$ symbol rather than $=$); you need to make an approximation. The approximation feels weird at first, but it is a useful trick.

4. It can be shown that van der Waal's equation is

$$\left[1 + p + \frac{3}{(1+v)^2}\right]\left[3\left(1+v\right) - 1\right] = 8\left(1+t\right)$$

   when put in terms of normalized variables. (This is hard to show, but you have learned enough to do it—you can try it for fun if you like.) With some more algebra this expression becomes

$$2p\left(1 + \frac{7v}{2} + 4v^2 + \frac{3v^3}{2}\right) = -3v^3 + 8t\left(1 + 2v + v^2\right).$$

   Use this last expression to obtain the critical isotherm exponent δ for a van der Waals gas. (Hints: (i) What is t on the critical isotherm? and (ii) use the result from the previous problem and problem 2b)

5. Write down Fick's and Fourier's laws for three dimensions. (Hint this is an easy question)

6. Determine the drop in blood pressure required to drive 0.2cc of blood through 1.0cm of artery (radius 0.5 mm) during a heartbeat (1s duration). Assume blood has a viscosity of 4 cp.

7. Given the Wiedemann, Frantz and Lorenz equation, what are the units of electrical conductivity κ_{el}?

8. Find the critical constants for the Dieterici equation of state. Verify that $z_c = 2/e^2$.

Conceptual Problems

9. Sketch the heat capacity as a function of temperature for a third order phase transition

10. Using symmetry guess the functional form for point source diffusion in three dimensions.

Computer Problems

11. Plot heat capacity near its critical point for the 3D Ising model (see table on p277 of notes). Work in terms of normalized variables.

12. Plot the coexistence curve near its critical point for the 3D spherical model and the 2D Ising model (see table on p277 of notes). Work in terms of normalized variables.

13. Visit the NIST webbook page form the PChem homepage. Click on "NIST Chemistry WebBook" and then on "Thermophysical Properties of Fluid Systems" set the pressure units to atm and the data type to isobaric properties. Press continue. Type in appropriate parameters such that the temperature range spans the liquid vapor phase transition. Determine the order of the phase transition based on the enthalpy and entropy graphs. Also download the data for C_P and C_V and use EXCEL plot both of these quantities versus temperature. Explain how C_P and C_V compare for the liquid phase and the vapor phase.

14. Visit the NIST webbook again and proceed like the previous problem. Now change the data type to isothermal properties. At what pressure does water go from a gas to a liquid when the system is at 298K? how about 370K? how about 400K?

① $\lim_{x\to\bar{x}} \left[\frac{x-\bar{x}}{\bar{x}} - \frac{x-\bar{x}}{x}\right] = \lim_{x\to\bar{x}} \frac{x(x-\bar{x}) - \bar{x}(x-\bar{x})}{\bar{x}\,x} = \frac{0}{\bar{x}^2} = 0$

so $\frac{x-\bar{x}}{\bar{x}} = \frac{x-\bar{x}}{x}$ in the limit $x\to\bar{x}$

② ⓐ $\lim_{x\to 0} \frac{x^3}{(x^3+x^2+x+1)} \sim \frac{x^3}{1} = x^{③}$ ← dominant exponent

ⓑ $\lim_{x\to 0} x^3(x^3+x^2+x+1) \sim x^3(1) = x^{③}$

③ $\nu = \frac{V-V_c}{V_c} \approx \frac{V-V_c}{V}$ (see problem #1)

$\nu \approx \frac{\frac{V}{m}-\frac{V_c}{m}}{\frac{V}{m}} = \frac{\frac{1}{\rho}-\frac{1}{\rho_c}}{\frac{1}{\rho}} = \frac{\frac{\rho_c-\rho}{\rho\rho_c}}{\frac{1}{\rho}} = \frac{\rho_c-\rho}{\rho_c}$

$\nu \approx -\bar{\rho}$

④ $2p\left(1+\frac{7\nu}{2}+4\nu^2+\frac{3\nu^3}{2}\right) = -3\nu^3+8t(1+2\nu+\nu^2)$

$t=0$ on critical isotherm

$2p = \frac{-3\nu^3}{\left(1+\frac{7\nu}{2}+4\nu^2+\frac{3\nu^3}{2}\right)}$ $p \sim \nu^3 \approx \bar{\rho}^{③}$ ← δ

so $\boxed{\delta = 3}$ for a vdW gas

⑤ Fick's 1st law $\frac{1}{A}\frac{\partial n}{\partial t} = -D\nabla C$

Fick's 2nd law $\frac{\partial C}{\partial t} = D\nabla^2 C$

Fourier's law $q_t = -K\nabla T$

⑥ Use Poiseville's Formula for liquid flowing through a tube

$\frac{\Delta V}{\Delta t} = \frac{\pi r^4 \Delta P}{8\eta l} \Rightarrow \Delta P = \frac{\Delta V\, 8\eta l}{\pi r^4 \Delta t}$

$\Delta P = \frac{6.2\,cm^3 \; 8 \; 4\times10^{-2}\frac{g}{cm\,s} \; 1.0\,cm}{\pi (0.05\,cm)^4 \; 1\,s} = 1.02\times10^4\,Pa$

⑦ The WFL eqn is

$\frac{K}{K_{el}T} = \mathcal{L} \Rightarrow K_{el} = \frac{K}{\mathcal{L}T}$

Units

$K_{el} = \frac{\left(\frac{J}{m K s}\right)}{\frac{V^2}{K^2}K} = \frac{J}{m\,s\,V^2}$ or $\frac{C}{m\,s\,V}$

⑧ Dieterici Eq: $P = \frac{RT e^{-\frac{a}{RTV_m}}}{V_m-b}$

at critical pt.

$P_c = \frac{RT_c e^{-\frac{a}{RTV_{mc}}}}{V_{mc}-b}$

Critical isotherm has an inflection at the critical point

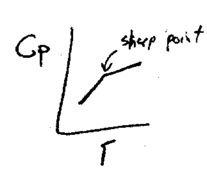
so $\left.\frac{dP}{dV}\right|_c = 0$ and $\left.\frac{d^2P}{dV^2}\right|_c = 0$

Use mathematica to solve the system of equations

$P_c = \frac{a}{4b^2e^2}$, $T_c = \frac{a}{4bR}$, $V_{mc} = 2b$

so $\boxed{Z = \frac{PV_m}{RT} = \frac{2}{e^2}}$ ✓

⑨



It is most appropriate to use spherical polar coordinates and take the point source as the origin. By symmetry there is no preferred direction of diffusion so the concentration must be independent of both θ and φ. It only depends on r. This reduces the problem to one dimension

so $c(r,t) \propto e^{-r^2/4Dt}$