

**Qualifying Examination**  
**Thermal Physics Solutions**  
**January 14, 2006**

**PROBLEM TA.**

In the dilute solution any of the solvent molecules can be replaced by a solute, so the entropy is

$$S = \ln \frac{N!}{(N-n)!n!} = N \ln \frac{N}{e} - (N-n) \ln \frac{N-n}{e} - n \ln \frac{n}{e} = -n \ln \frac{\rho}{e}$$

Using the identity  $\frac{\partial S}{\partial V} = \frac{\partial P}{\partial T}$  and the fact that  $V \propto N$  for the osmosis process, we get  $V \frac{\partial S}{\partial V} = N \frac{\partial S}{\partial N} = n$  and thus  $P = Tn/V$

**PROBLEM TB.**

The naive way of heating the house by transforming the electrical energy,  $E$ , into heat,  $Q$ , is worse than to use reversed Carnot engine that consumes work  $W = E$  and heat  $Q_{out} = ST_0$  from the outside to produce heat  $Q = ST = E + ST_0$  in the inside. In this case one gets  $Q = \frac{T}{T-T_0}E$  for the same energy cost  $E$ . It is also the most efficient way because in case a more efficient way existed, a second Carnot engine working in the normal direction would produce enough energy to feed the reverse one and to heat the house at no energy cost violating the second law of thermodynamics.

**PROBLEM TC1.**

Local stability implies that the pressure difference is compensated by the gravitational force:  $dP/dz = -g\rho = -P\mu g/RT$ . Global stability implies that the cyclic process does not produce positive work. The process consists in adiabatic expansion (upward motion), isobaric cooling (temperature equilibration), adiabatic compression (downward motion) and isobaric heating. Assume that the temperature and pressure at the bottom is  $T_b, P_b$  while at the top they are  $T_t, P_t$ . The temperature of the air after the first stage is  $T'_t = T_b(P_t/P_b)^{1/c_p}$ , the volume  $V' = V_0(P_t/P_b)^{1/c_p-1}$ . The work done by the air during this process is positive because  $V' > V_0$  provided that the pressure at higher altitude is less as it should according to the local stability condition. At the next stage the air cools down or is heated up depending on the relation between  $T'_t$  and  $T_t$  if  $T'_t < T_t$  the air is heated and expands further to volume  $V'' = V'(T_t/T'_t)$  doing more work. At the next stage the air is adiabatically compressed and finally is cooled down. The work done at this stages is in this case neagtive and larger in magnitude than positive work; the whole process is equivalent to reversed Carnot engine. In the opposite case of  $T'_t > T_t$  the air cools down and does negative work at the second stage of the process, so the whole cycle is equivalent to Carnot engine running in the positive direction. In this case mechanical work can be produced and thus the atmosphere is unstable. Thus, we get the condition that atmosphere is stable iff  $T_b(P_t/P_b)^{1/c_p} \leq T_t$ . In a differential form  $dT/dz \leq \frac{T}{c_p P} dP/dz = \frac{\mu g}{c_p R} = 9.7K/km$ . As expected, the typical atmosphere is close to the instability but stable.

**PROBLEM TC2.**

Energy conservation implies that  $U_i + P_i V_i = U_f + P_f V_f$  so the process happens at constant enthalpy:  $dH = TdS + VdP = 0$ . Expressing the entropy change in the variables  $(T, P)$  we get  $dS = C_p \frac{dT}{T} - \frac{\partial V}{\partial T} dP$ . Thus,

$$C_p dT - T \frac{\partial V}{\partial T} dP + V dP = 0$$

or

$$\frac{dT}{dP} = \frac{1}{C_p} \left( T \frac{\partial V}{\partial T} - V \right)$$

Van-der-Waals gas satisfies the equation

$$\left( P + a \frac{N^2}{V^2} \right) (V - Nb) = NkT$$

At low densities it can be simplified:

$$V = \frac{NkT}{P} \left( 1 + b \frac{P}{kT} - a \frac{P}{(kT)^2} \right)$$

so

$$\frac{dT}{dP} = \frac{T}{C_p} \frac{Nk}{P} \left( -b \frac{P}{kT} + 2a \frac{P}{(kT)^2} \right) = \frac{1}{kc_p} \left( \frac{2a}{kT} - b \right)$$

### PROBLEM TD1.

The position of the end is the sum of the link displacements:  $\vec{x} = \sum \vec{u}_k$ , so the energy of the molecule subjected to the force  $E = -\vec{f} \cdot \vec{x}$  is the sum of the energies of individual links  $E = -\sum \vec{f} \cdot \vec{u}_k$ . The free energy can be obtained from the partition function

$$\mathcal{F} = -T \ln \left( \int d\hat{u} e^{\beta \vec{f} \cdot \vec{u}} \right)^N = -NT \ln \left( 2\pi \int_{-1}^1 dz e^{\beta flz} \right) = -NT \ln \left( 4\pi \frac{\sinh \beta fl}{\beta fl} \right)$$

The average distance between the ends

$$\langle \vec{x} \rangle = -\frac{d\mathcal{F}}{d\vec{f}} = Nl \left( \coth \beta fl - \frac{1}{\beta fl} \right) \frac{\vec{f}}{f} \approx \frac{1}{3T} Nl^2 \vec{f}$$

where last approximate equality holds in the linear regime.

### PROBLEM TD2.

Phase equilibrium implies that the chemical potentials of the gas and liquid are equal:  $\mu_l = \mu_g$ . Differentiating this equation along the phase equilibrium line we get (as in the derivation of Clausius-Clapeyron equation)

$$\frac{dP}{dT} = \frac{s_g - s_l}{v_g - v_l}$$

Because  $v_g \gg v_l$  the denominator in this formula is dominated by the volume per one gas molecule and does not exhibit any features at the normal-superfluid transition that affects only liquid. The same applies to the entropy  $s_g$  per one gas molecule. According to Landau theory of phase transitions, the free energy density of the system near transition is  $F = \alpha(T - T_c)\Psi^2 + \frac{1}{2}\beta\Psi^4$  where  $\Psi$  is the order parameter. The nature of the order parameter is irrelevant for this problem because for any order parameter the free energy acquires additional contribution  $F = -(\alpha(T - T_c))^2/2\beta$  below  $T_c$  and thus the entropy per one molecule acquires a contribution  $\Delta s = \alpha^2(T - T_c)v_l/\beta$ . Thus, below the transition the derivative of the phase equilibrium line acquires additional term

$$\frac{dP}{dT} = \left( \frac{dP}{dT} \right)_0 + \frac{\alpha^2(T_c - T)v_l}{\beta v_g} = \left( \frac{dP}{dT} \right)_0 + \frac{\alpha^2(T_c - T)\mu P_0}{\beta \rho R T_c}$$

Due to fluctuations, the linear  $(T_c - T)$  dependence is replaced by a power law  $(T_c - T)^{1-\chi}$ .