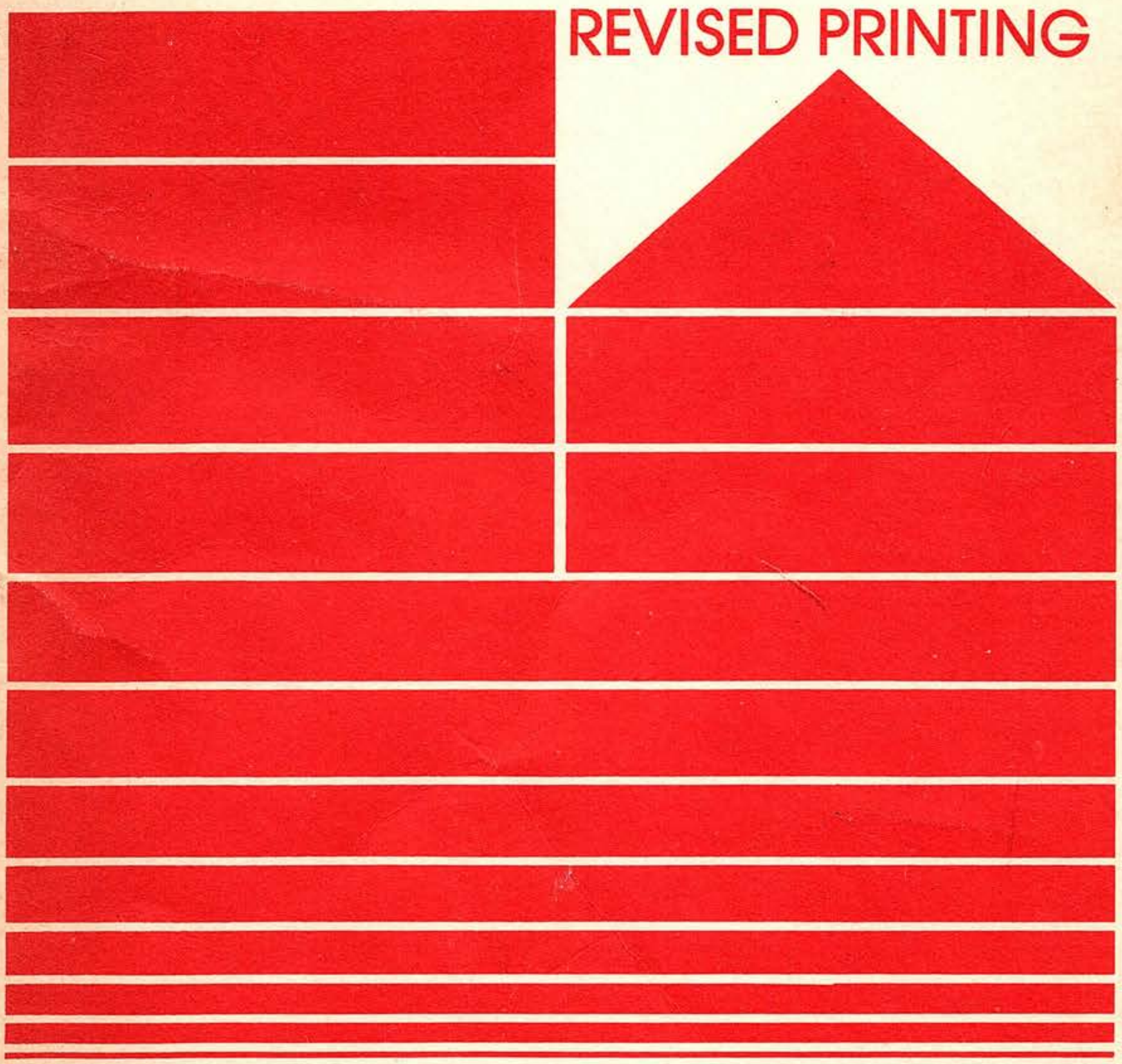
Solutions Manual to accompany

Statistical Thermodynamics

REVISED PRINTING



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Solutions Manual to accompany STATISTICAL THERMODYNAMICS

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Chapter 1

1.1

Test	$S = K_1(NUV)^{1/3}$	$S = K_2\left(\frac{V^3}{NU}\right)$	$U = K_3\left(\frac{S^2}{V}\right)e^{S/NR^\circ}$
Continuous differentiable function of U, V, N?	Yes	Yes	Yes
S additive in N	Yes	Yes	Yes
S monotonically increasing function of U	Yes	No	Yes
S vanishes with $\frac{\partial U}{\partial S}\Big\|_{N,V}$	Yes	No	Yes
Conclude that purported fundamental eq. is	legit.	<u>not</u> legit.	legit.

1.2

1.) $p \equiv T\frac{\partial S}{\partial N}\Big|_{V,N} = \frac{NR^\circ T}{V}$; $\underline{pV = NR^\circ T}$

2.) $T = \frac{\partial U}{\partial S}\Big|_{V,N} = \left[\frac{7}{2}\frac{NR^\circ}{U}\right]^{-1}$; $\underline{U = \frac{7}{2}NR^\circ T}$

& for good measure

3.) $\mu = -T\frac{\partial S}{\partial N}\Big|_{U,V} = \underline{-\frac{S_0}{N_0}T - R^\circ T\left[\left(\frac{U}{U_0}\right)^{\frac{7}{2}}\frac{V}{V_0}\left(\frac{N_0}{N}\right)^{9/2}\right] + \frac{7}{2}R^\circ}$

1.3 Substituting values for U & S from Eqs. (1.24) & (1.23) into $F = U - TS$ gives:

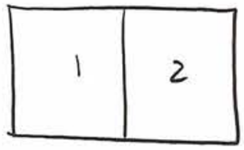
$$\underline{F(T,V,N) = NR^\circ T\left\{\frac{F_0}{N_0R^\circ T_0} - \ln\left[\left(\frac{T}{T_0}\right)^{3/2}\frac{V}{V_0}\left(\frac{N_0}{N}\right)^{5/2}\right]\right\}}$$

and the equations of state are:

$$\underline{p(T,V,N) = -\frac{\partial F}{\partial V}\Big|_{T,N} = \frac{NR^\circ T}{V}}$$

$$\underline{\mu(T,V,N) = \frac{\partial F}{\partial N}\Big|_{T,V} = R^\circ T\left\{\frac{F_0}{N_0R^\circ T_0} - \ln\left[\left(\frac{T}{T_0}\right)^{3/2}\frac{V}{V_0}\left(\frac{N_0}{N}\right)^{5/2}\right] + \frac{5}{2}\right\}}$$

$$\underline{S(T,V,N) = -\frac{\partial F}{\partial T}\Big|_{V,N} = NR^\circ\left\{\frac{-F_0}{N_0R^\circ T_0} + \ln\left[\left(\frac{T}{T_0}\right)^{3/2}\frac{V}{V_0}\left(\frac{N_0}{N}\right)^{5/2}\right] + \frac{3}{2}\right\}}$$

1.4 

$V_1 + V_2 = \text{const}$; $dV_1 = -dV_2$

$$dS = dS_1 + dS_2 = \frac{\partial S_1}{\partial V_1} dV_1 + \frac{\partial S_2}{\partial V_2}(-dV_1) = 0$$

$\therefore \frac{\partial S_1}{\partial V_1} = \frac{\partial S_2}{\partial V_2}$ or $\frac{p_1}{T_1} = \frac{p_2}{T_2}$, but $T_1 = T_2$ since The barrier is diathermal. We conclude that $\underline{\underline{p_1 = p_2}}$

1.5 This time $N_1 + N_2 = \text{Const.}$ so $dN_1 = -dN_2$ where N is the number of moles of the substance to which the barrier is permeable. Then

$$dS = \frac{\partial S_1}{\partial N_1} dN_1 + \frac{\partial S_2}{\partial N_2}(-dN_1) = 0 \quad \text{or} \quad \frac{\partial S_1}{\partial N_1} = \frac{\partial S_2}{\partial N_2}$$

Thus $-\frac{\mu_1}{T_1} = -\frac{\mu_2}{T_2}$ where μ is the chemical potential of the substance to which the barrier is permeable. But $T_1 = T_2$ since the barrier is diathermal, so in this case $\underline{\underline{\mu_1 = \mu_2}}$

1.6 The result is given in Eq. (1.46): $\underline{-\frac{F}{T}(\frac{1}{T}, V, N) = S - \frac{1}{T}U}$. It can be obtained using $d(U\frac{1}{T}) = U d(\frac{1}{T}) + \frac{1}{T} dU$ to change the single dep. var. from U to $1/T$. Finally we form derivatives noting that $-\frac{F}{T}(\frac{1}{T}, V, N) = S(U,V,N) - \frac{U}{T}$

$$\underline{\frac{\partial(-F/T)}{\partial(1/T)} = -U} \; ; \; \underline{\frac{\partial(-F/T)}{\partial V} = \frac{\partial S}{\partial V} = \frac{p}{T}} \; ; \; \underline{\frac{\partial(-F/T)}{\partial N} = \frac{\partial S}{\partial N} = -\frac{\mu}{T}}$$

1.7 Use $C_V = \frac{3}{2}R^\circ$ then $U_{1_i} = 2\frac{3}{2}(250)R^\circ$, $U_{2_i} = 3\frac{3}{2}(350)R^\circ$. $U = U_{1_i} + U_{2_i} = 2325 R^\circ = \text{const.}$, $T_f = \frac{U}{\frac{3}{2}R^\circ N} = \frac{2325}{1.5 \cdot 5}$. so $\underline{T_f = 310^\circ K}$. $\underline{U_{1_f} = 2\frac{3}{2}R^\circ(310) = 930 R^\circ}$, $\underline{U_{2_f} = 1395 R^\circ}$

1.8 First compute N_1 & N_2: $N_1 = \frac{pV}{R^\circ T} = \frac{\frac{1}{2}\cdot 1000}{.08205(273+20)} = 20.8$ g moles

and $N_2 = \frac{1\times 1000}{.08205(273+80)} = 34.4$ g moles. $N_1 + N_2 = 55.2$ g moles

Then $U = U_{1_i} + U_{2_i} = \frac{3}{2}R^\circ[20.8(293) + 34.4(353)] = 54{,}400$ cal.

so $T_f = \frac{U}{\frac{3}{2}R^\circ(N_1+N_2)} = 330\,^\circ K = \underline{57\,^\circ C}$

And $p_f = (N_1+N_2)R^\circ(330)/(1000+1000) = \underline{0.746 \text{ atm}}$

1.9 Since N and p are constant, it is convenient to use

$$dH = TdS + V\underbrace{dp}_{=0} + \mu \underbrace{dN}_{=0}$$

Thus: $Q = \int TdS = \Delta H = \Delta(U + pV) = \Delta(\frac{3}{2}\underbrace{R^\circ T}_{=pV} + pV)$

$$Q = \frac{5}{2}\Delta(pV) = \frac{5}{2}(50\times 1 - 20\times 1) = 75 \text{ liter-atm}$$

$$= \underline{\underline{1815 \text{ cal}}}$$

1.10 $d\left(\frac{pV}{T}\right) = d\left\{S(U,V,N) - \frac{U}{T} + \frac{N\mu}{T}\right\}$. Now, noting that the natural variables of $\frac{pV}{T}$ are $\frac{1}{T}$, V, and $\frac{\mu}{T}$, we get

$$d\left(\frac{pV}{T}\right) = -U\,d\left(\frac{1}{T}\right) + \underbrace{\frac{\partial S}{\partial V}}_{\frac{p}{T}} dV + N\,d\left(\frac{\mu}{T}\right)$$

so: $\underline{\frac{\partial \frac{pV}{T}}{\partial(1/T)} = -U}$ $\quad \underline{\frac{\partial \frac{pV}{T}}{\partial V} = \frac{p}{T}}$ $\quad \underline{\frac{\partial \frac{pV}{T}}{\partial(\mu/T)} = N}$

and for, say a monatomic ideal gas, the diff. Eq. becomes

$$d\left(\frac{pV}{T}\right) = +R^\circ N d\ln T^{3/2} + R^\circ N d\ln V + R^\circ N d\ln \frac{N}{T^{3/2}V}$$

$$= R^\circ dN \quad \text{so} \quad \frac{pV}{T} = R^\circ N$$

1.11 Substitute $\mu = \left.\frac{\partial F}{\partial N}\right|_{T,V} = kT - kT\ln\left(\frac{Z}{N}\right)$ in the Euler relation: $\Psi = F - \mu N = -pV$ and obtain

$$\Psi = -NkT\ln\left(\frac{Z}{N}\right) - \left[kT - kT\ln\left(\frac{Z}{N}\right)\right]N = -pV = f(T, V, N[T,V,\mu])$$

$$\text{Hence: } \quad \Psi = \Psi(T,V,\mu) = F - \mu N$$

1.12 We have $\lim_{T\to 0} S = 0$, and in an isochoric process, $S = \int_0^T (c_v/T)\,dT$. Let us express $c_v = \sum_{i=0}^{\infty} a_i T^i$. Then $S = a_0 \ln(T/0) + a_1 T + a_2 T^2 + \cdots$. Hence a_0 must be zero near $T=0$ and $c_v \to 0$ as $T \to 0$.

1.13 $$df(T,v) = \underbrace{\left.\frac{\partial f}{\partial T}\right|_v}_{-S} dT + \underbrace{\left.\frac{\partial f}{\partial v}\right|_T}_{-p = \frac{a}{v^2} - \frac{RT}{v-b}} dv \qquad ①$$

$$\left(\text{but } \left.\frac{\partial(-S)}{\partial T}\right|_v = -\frac{C_v(T)}{T} = -\frac{A}{T} - B\right.$$

$$\text{so } \quad -S = -A\ln T - BT + F_1(v) \qquad ②$$

now integrate the two differential coefficients & get

① $\quad f = -\frac{a}{v} - RT\ln(v-b) + F_2(T)$

② $\quad f = AT - AT\ln T - \frac{B}{2}T^2 + F_1(v)T + F_3(v)$

Comparing these we obtain $F_1 = -R\ln(v-b)$, $F_3 = -\frac{a}{v}$,

$$F_2 = AT - \frac{B}{2}T^2 - AT\ln T$$

so

$$\underline{\underline{f(T,v) = AT(1-\ln T) + \frac{B}{2}T^2 - RT\ln(v-b) - \frac{a}{v}}} + \text{Const.}$$

CHAPTER 2

2.1) $$p_{ij} = \int (mu_j)\, u_i f \, d\Omega = \begin{vmatrix} \rho\overline{u^2} & \rho\overline{uv} \\ \rho\overline{vu} & \rho\overline{v^2} \end{vmatrix}$$

Since from symmetry, $\rho\overline{u^2} = \rho\overline{v^2}$,

$$\rho\overline{C^2} = \rho(\overline{u^2} + \overline{v^2}) = 2\rho\overline{u^2} = 2p \;; \quad \underline{\underline{p = \frac{\rho\overline{C^2}}{2}}}$$

and since $\rho = m \cdot n$, $\quad \underline{\underline{p = n \cdot \frac{m\overline{C^2}}{2} \equiv K}}$

2.2) $$\overline{C^2} = \frac{1}{n}\int_0^{C_{max}} c^2 f(c)\, dc = \frac{6n}{nc_{max}^3}\int_0^{C_{max}} (C^3 C_{max} - C^4)\, dc = \underline{\underline{\frac{3}{10} C_{max}^2}}$$

$\langle C \rangle$, the average of c over space and velocity is the same as $\overline{C}$ in this case since f does not vary in space.

2.3) $$J_{molecules} = \frac{n\overline{C}}{4} = n\sqrt{\frac{kT}{2\pi m}} = \frac{p}{kT}\sqrt{\frac{kT}{2\pi m}} = \frac{p}{\sqrt{2\pi (M/N_A) kT}}$$

$$= \frac{1.013 \times 10^6 \ \frac{gm\text{-}cm}{sec^2} / cm^2}{\sqrt{6.28 \ \frac{29}{6.02 \times 10^{23}} \ \frac{gm}{Molecule} \ 1.38 \times 10^{-16} \ \frac{\frac{gm\text{-}cm^2}{sec^2}}{molecule\,^\circ K} \ 300^\circ K}}$$

$$\underline{\underline{J_{molecules} = 2.862 \times 10^{23} \ molecule/cm^2 \, sec}}$$

2.4) a.) $$n = \frac{p}{kT} = \frac{1.013 \times 10^6}{(1.38 \times 10^{-16})(373)} = \underline{\underline{1.97 \times 10^{19} \ molecule/cm^3}}$$

b.) With reference to problem 2.3 $\Big\}$ $$J_{molec.} = J_{molec.}\sqrt{\frac{M_{air} T_{air}}{M_{H_2O} T_{H_2O}}}$$

So $$J_{molecules} = 2.862 \times 10^{23}\sqrt{\frac{29(300)}{18(373)}} = \underline{\underline{3.258 \times 10^{23} \ \frac{molecules}{cm^2 \, sec}}}$$

c.) $J_{evaporation} = J_{condenstation}$ at equilibrium

$$= \underline{\underline{3.258 \times 10^{23} \ \frac{molecules}{cm^2 \, sec}}}$$

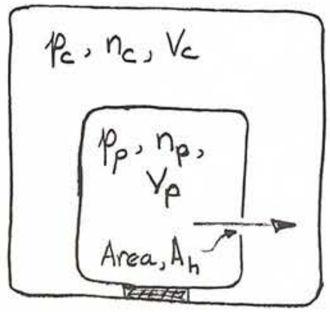
2.4) d.) $\overline{KE} = \frac{3}{2}kT = 1.5\left(1.38\times10^{-23}\,\frac{\text{Joule}}{\text{molec.}\,^\circ K}\right)\left(\overset{373^\circ K}{\cancel{300^\circ K}}\right) = 7.74\times(10)^{-21}\,\frac{\text{Joule}}{\text{molec.}}$

while the energy required to evaporate a molecule is

$$\frac{2250\text{ Joule}}{\text{gm}}\;\frac{18\text{ gm}}{\text{gm-mole}}\;\frac{\text{gm-mole}}{6.02\times10^{23}\text{ molec.}} = 6.75\times10^{-20}\,\frac{\text{Joule}}{\text{molec.}}$$

The energy required to give the molecule its KE is thus only $(0.774/6.75)$ or 11.5 % of the latent heat. Most of the latent heat goes to break the strong attractive forces that hold the liquid molecules together.

2.5)



$$V_p\frac{dn_p}{dt} = -\frac{(n_p-n_c)\bar{c}}{4}A_h = -V_c\frac{dn_c}{dt}$$

$$\frac{d^2n_p}{dt^2} = -\frac{A_h\bar{c}}{4V_p}\left[\frac{dn_p}{dt} - \underbrace{\frac{dn_c}{dt}}_{=\frac{A_h\bar{c}}{4V_c}(n_p-n_c)}\right]$$

but $V_pn_p + V_cn_c = V_pn_{p_i}$

so
$$\frac{d^2n_p}{dt^2} + \left[\frac{A_h\bar{c}}{4V_p}\right]\frac{dn_p}{dt} - \left[\left(\frac{A_h\bar{c}}{4V_p}\right)^2\frac{V_p}{V_c}\left(1+\frac{V_p}{V_c}\right)\right]n_p = -\left(\frac{A_h\bar{c}}{4V_p}\right)^2\frac{V_p}{V_c}n_{p_i}$$

with conditions: $n_p(t=0) = n_{p_i}$; $n_p(t=\infty) = \frac{V_p}{V_c+V_p}n_{p_i}$.

The solution subject to these conditions is:

$$n_p = \frac{n_{p_i}}{1+\frac{V_c}{V_p}} + \frac{n_{p_i}}{1+\frac{V_p}{V_c}}\exp\left(-\left[\frac{A_h\bar{c}}{8V_p} + \sqrt{\frac{1}{4}\left(\frac{A_h\bar{c}}{4V_p}\right)^2 + \left(\frac{A_h\bar{c}}{4V_p}\right)^2\frac{V_p}{V_c}\left(1+\frac{V_c}{V_p}\right)}\right]t\right)$$

$$\underline{\underline{p_p = p_{p_i}\left\{\frac{1}{1+\frac{V_c}{V_p}} + \frac{1}{1+\frac{V_p}{V_c}}\exp\left[-\frac{A_h\bar{c}}{8V_p}\left(1+\sqrt{1+4\left(\frac{V_p}{V_c}+\left(\frac{V_p}{V_c}\right)^2\right)}\right)t\right]\right\}}}$$

$$\left\{\lim_{V_c\to\infty} p_p = p_{p_i}\exp\left[-\frac{A_h\bar{c}}{4V_p}\,t\right]\right\}$$

Finally

$$\underline{\underline{p_c = n_ckT = \frac{V_p}{V_c}(p_{p_i} - p_p)}}$$

2.6 This is a special case of problem 2.5

2.7 Eq. of motion: $\ddot{x} + \frac{c}{m}\dot{x} + \frac{k}{m}x = 0$, Initial conditions are unspecified so we shall arbitrarily do the case for which $x(0)=0$, $\dot{x}(0) = 1$ ft/sec. The solution is:

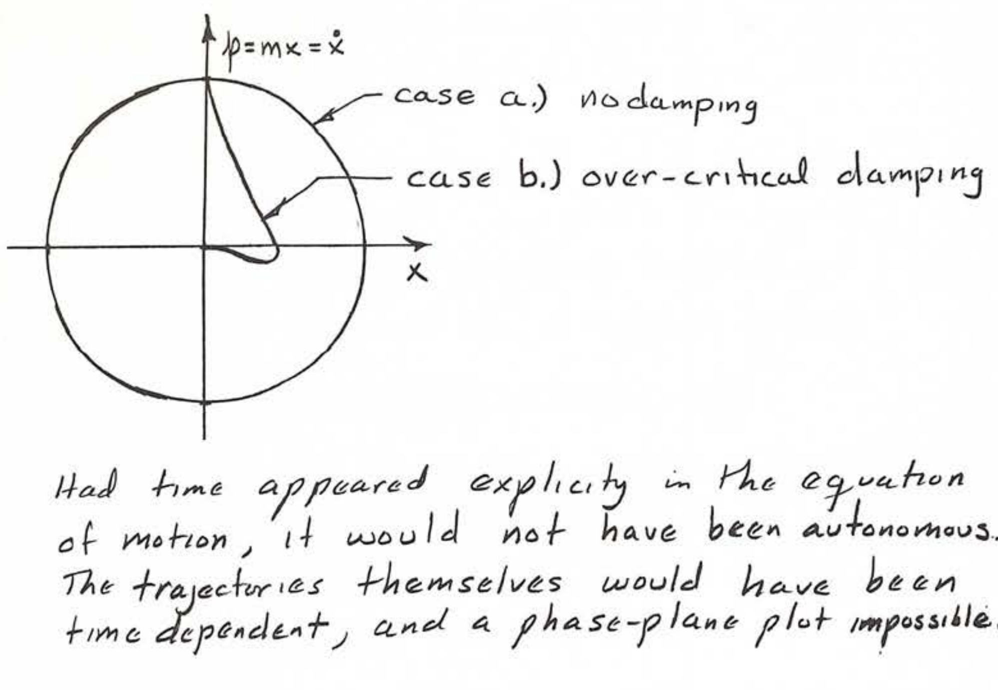
$$\underline{x = \frac{e^{-c/2m}}{\sqrt{\left(\frac{c}{2m}\right)^2 - \frac{k}{m}}} \sinh\left(\sqrt{\left(\frac{c}{2m}\right)^2 - \frac{k}{m}}\ t\right)}$$

a.) $k = 1\,lb_f/ft$, $m = 1\,lb_f\,sec^2/ft$, $c = 0$

$$\left.\begin{aligned} x &= \frac{1}{2i}(e^{it} - e^{-it}) = \sin t \\ \dot{x} &= \cos t \end{aligned}\right\}$$ parametric eqns. for a circle of 1 ft radius.

b.) $k=1$, $m=1$, $c=\sqrt{8}\,lb_f/ft/sec$

$$\left.\begin{aligned} x &= e^{-\sqrt{2}t}\sinh t \\ \dot{x} &= -\sqrt{2}\,e^{-\sqrt{2}t}\sinh t + e^{-\sqrt{2}t}\cosh t \end{aligned}\right\}$$ assume values of t and solve for x and $\dot{x}$



Had time appeared explicity in the equation of motion, it would not have been autonomous. The trajectories themselves would have been time dependent, and a phase-plane plot impossible.

2.8) $\frac{1}{N} f_{normal} = F(x) = \frac{\exp(-x^2/2\sigma^2)}{\sqrt{2\pi}\,\sigma}$

and $\int_{-\infty}^{\infty} F(x)\,dx = \frac{1}{\sqrt{2\pi}\,\sigma}\sqrt{2}\sigma \int_{-\infty}^{\infty} e^{-\phi^2} d\phi = \frac{1}{\sqrt{\pi}}\left(2\frac{\sqrt{\pi}}{2}\right) = \underline{\underline{1}}$

since the integral of F over the range of its argument is unity, it is normalized.

2.9) The distance, l, of the piston above the bottom of the cyl. is determined by an energy balance

$$\frac{1}{2}mc^2 = \frac{1}{2}Mgl$$

a.) Now pressure, $p = \frac{Mg}{A}$ and Volume $= Al$ so

$$pV = \frac{Mg}{A} Al = Mgl \quad \text{or} \quad \underline{\underline{pV = mc^2}}$$

For an ideal gas $pV = \frac{n}{3} m\overline{c^2}$, but in this case $V \Leftrightarrow v/n$ and $c^2 \Leftrightarrow \overline{c^2}$. The expression then differs by a factor of three because in a gas there are three directions of motion, only one of which contributes to pressure. Here <u>all</u> the motion contributes to pressure

b. The velocity of the sphere after a collision is $(c - v_p) - v_p = c - 2v_p$. The change in KE is (for one collision) $\frac{1}{2}m(c-2v_p)^2 - \frac{1}{2}mc^2 \simeq -2mv_pc$. The loss of energy in δt or in $\delta t/(2l/c)$ collisions is

$$-\frac{c\,\delta t}{2l} \cdot 2mv_pc = -\frac{mc^2}{l}(v_p\,\delta t) = -\frac{mc^2}{l}dl = -Mg\,dl$$

but $p = \frac{Mg}{A}$ so $\underline{\delta KE = -p\,A\,dl = -p\,dV}$

which is exactly the work done by a gas.

2.10) The first law for an adiabatic ideal gas expansion is

$$\frac{T_o}{T_1} = 1 + \frac{\gamma-1}{2} \frac{V_1^{\,2}}{\gamma R^\circ T_1}$$

where T_o is stagnation temperature. Thus

$$T_o = T_1 + \frac{\gamma-1}{2} \frac{V_1^{\,2}}{\gamma R^\circ}$$

when the gas has been expanded completely, $T_1 = 0$ and $V_{1\,max} = \sqrt{\dfrac{2\gamma R^\circ T}{\gamma-1}}$

But $V_{rms} = \sqrt{3R^\circ T}$ so $\underline{\dfrac{V_{1\,max}}{V_{rms}} = \sqrt{\dfrac{2\gamma}{3(\gamma-1)}}}$

for the two velocities to be equal $\underline{\gamma \text{ must} = 3}$. But $\gamma = \frac{D+2}{D}$, so this would correspond with 1 degree of freedom. Actually the gas moves faster than the molecules since the original gas contributes 3, not just 1, modes of of energy storage to the velocity of the perfectly ordered flow at 0°K.

2.11) $\underline{C_{rms} = \sqrt{3R^\circ T}}$, Eq. (2.35); $\underline{\bar{C} = \sqrt{\dfrac{8R^\circ T}{\pi}}}$, Eq. (2.48)

and $\left.\dfrac{df}{dc}\right|_{C_m} = 0 = 4n\pi\left(\dfrac{m}{2\pi kT}\right)^{3/2} e^{-\frac{mC_m^2}{2kT}}\left[2C_m - \dfrac{mC_m^3}{kT}\right]$

so $\underline{C_m = \sqrt{2R^\circ T}}$

and

$$\underline{C_m : \bar{C} : C_{rms} :: \sqrt{2} : \sqrt{\tfrac{8}{\pi}} : \sqrt{3} \;\tilde{::}\; 1 : 1.13 : 1.22}$$

2.12) $$\overline{U^2} = \int_0^\infty U^2 f(U)\,dU = \sqrt{\frac{m}{2\pi kT}}\left(\frac{2kT}{m}\right)^{3/2}\underbrace{\int_0^\infty \phi^2 e^{-\phi}\,d\phi}_{\sqrt{\pi}/4} = \underline{\underline{\frac{R^\circ T}{2}}}$$

It would have been easier to recall that

$$\tfrac{1}{2}m\overline{U^2} = \frac{kT}{2} \quad \text{so} \quad \overline{U^2} = \frac{R^\circ T}{2}$$

2.13) The first part of this problem is largely one of definition. As defined, ψ is exactly the Maxwell speed distribution. If we recall that $C_m^2 = 2kT/m$ then:

$$\underline{\psi(C) \equiv f(C) = \frac{4}{C_m^3\sqrt{\pi}}\, C^2 \exp(-\alpha^2)}$$

fraction w/speed $> C$ is $1 - \int_0^\alpha \frac{4}{\sqrt{\pi}}\alpha^2 \exp(-\alpha^2)\,d\alpha$

$$= 1 - \frac{4}{\sqrt{\pi}}\left[\frac{1}{2}\int_0^\alpha e^{-\alpha^2}d\alpha - \frac{\alpha e^{-\alpha^2}}{2}\right]$$

$$= \underline{1 + \frac{2\alpha}{\sqrt{\pi}}e^{-\alpha^2} - \operatorname{erf}\alpha}$$

But erf α decays more rapidly with increasing α than $\alpha e^{-\alpha^2}$ does. Hence it may be neglected for $\alpha > 1.5$. Noting that $\alpha = \sqrt{\frac{mC^2}{2kT}}$ we then get

$$\text{fraction with speed} > C \simeq \underline{1 + \frac{2}{\sqrt{\pi}}\sqrt{\frac{mC^2}{2kT}}\, e^{-\frac{mC^2}{2kT}}}$$

2.14) $\wp(C) = 4\pi C^2\left[\frac{m}{2\pi kT}\right]^{3/2}\exp\left(-\frac{mC^2}{2kT}\right)dC$, but $C = \sqrt{\frac{2E}{m}}$ so

$$\wp(E) = \underbrace{\frac{8\pi E}{m}\left[\frac{m}{2\pi kT}\right]^{3/2}\exp\left(-\frac{E}{kT}\right)\sqrt{\frac{1}{2mE}}}\, dE$$

$$\underline{f(E) = 2\pi(\pi kT)^{-3/2}\sqrt{E}\,\exp(-E/kT)}$$

2.14 cont'd.) $\left.\frac{df}{dE}\right|_{E_m} = 0 = 2\pi(\pi kT)^{-3/2}\left[\frac{\exp(-\frac{E}{kT})}{2\sqrt{E}} - \frac{\sqrt{E}\exp(-\frac{E}{kT})}{kT}\right]$

so $\underline{\underline{E_m = kT/2}}$

for fission neutrons, $T = \frac{2}{3k}E_{rms} = \frac{2\ {}^\circ K}{1.38\times10^{-16}erg} \cdot \frac{2\times10^6 ev\ erg}{.625\times10^{12} eV}$

$\underline{\underline{T = 1.55\times10^{10}\ {}^\circ K}}$,

an immense "Temperature"

2.15) This is an uncomplicated numerical substitution problem and possible computer exercise. C_m, $\bar{C}$, and C_{rms} are $\underline{C_m = 1.5\times10^5 cm/sec}$, $\underline{\bar{C} = 1.691\times10^5 cm/sec}$, and

$\underline{C_{rms} = 1.838\times10^5 cm/sec}$

2.16) $n = \int_{-\infty}^{\infty} a^3 n\exp(b[U^2+V^2+W^2])\,dU\,dV\,dW = a^3 n\left(\frac{1}{-b}\right)^{3/2}(\sqrt{\pi})^3$

$T = \frac{ma^2n}{3kn}\int_0^{\infty}(U^2+V^2+W^2)\exp(U^2+V^2+W^2)dU\,dV\,dW = \frac{ma^3}{3k}\,\frac{3}{2}\,\frac{\pi^{3/2}}{(-b)^{5/2}}$

so $a^3 = (-b/\pi)^{3/2}$; $T = \frac{m}{3k}\left(-\frac{b}{\pi}\right)^{3/2}\frac{3(\sqrt{\pi})^3}{2(-b)^{5/2}}$

so $\underline{\underline{b = -\frac{m}{2kT}}}$ $\underline{\underline{a = \frac{m}{2\pi kT}}}$

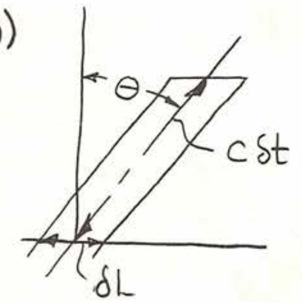
2.17) $J_{molecules} = \int_0^{\infty}\int_{\theta=0}^{\pi/2}\int_{\phi=0}^{2\pi} n\left(\frac{m}{2\pi kT}\right)^{3/2} c^3\exp\left(-\frac{mc^2}{2kT}\right)\sin\theta\cos\theta\, d\phi\, d\theta\, dc$

$= n\left(\frac{m}{2\pi kT}\right)^{3/2}\underbrace{\left[\phi\right]_0^{2\pi}}_{2\pi}\underbrace{\left[\frac{\sin^2\theta}{2}\right]_0^{\pi/2}}_{1/2}\frac{1}{2\left(\sqrt{\frac{m}{2kT}}\right)^4} = \underline{\underline{n\sqrt{\frac{kT}{2\pi m}}}}$

2.18) $\tau = \rho\overline{UV} = \rho\frac{1}{n}\int UV f(\vec{C})\,d\Omega$

But $f(\vec{C}) \sim e^{-mU^2/2kT} e^{-mV^2/2kT}$ so the integrand is an odd function and its integral from $-\infty \to +\infty$ vanishes. Thus $\underline{\tau = 0}$. The question as to the existence of viscosity is moot. There is no shear because there are no gradients. If there were any gradients of velocity there would be viscosity but the gas would be deviating from Maxwellian behavior. It would be fair to say that in the Maxwellian limit, μ is finite.

2.19)



$d\Omega = d\theta\, C\, dC$

vol of 2-dim cyl $= C\cos\theta\,\delta t\,\delta L$

$$J = \frac{1}{\delta t\,\delta L}\int f\,C^2\cos\theta\,dC\,\delta L\,\delta t$$

$$= \int_{-\pi/2}^{\pi/2}\cos\theta\,d\theta\int_0^\infty C^2 f\,dC = 2\int_0^\infty C^2 f\,dC$$

but $n\bar{C} = \int C^2 f\,dC\,d\theta = 2\pi\int_0^\infty C^2 f\,dC$

combining, $\underline{\underline{J = 2\frac{n\bar{C}}{2\pi} = \frac{n\bar{C}}{\pi}}}$

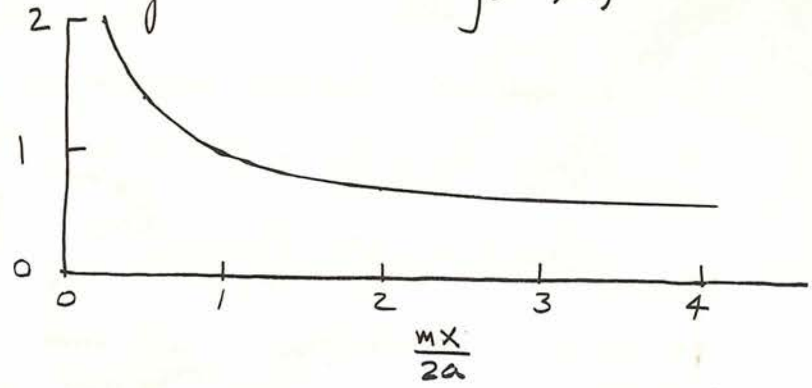
2.20) $F = m\frac{d^2x}{dt^2}$ or $\frac{d^2x}{dt^2} = -\frac{a/m}{x^2}$

reduce to two first order d.e.s $\Big\}$ $\quad \dot{x} \equiv y$

$\dot{y} = -\frac{a_m}{x^2}$

2.20 cont'd.) so $\frac{dy}{dx} = \frac{\dot{y}}{\dot{x}} = -\frac{am}{y x^2}$

separate variables and integrate: $\underline{y = \sqrt{\frac{2a}{mx}}}$
(constant of int. = 0 since $y(x=\infty)=0$)



2.21) Max. q would occur if all molecules falling on the condensing sheet adhered to it:

$$q_{max} = m \frac{\text{lbm}}{\text{Molec.}}\, h_{fg} \frac{\text{Btu}}{\text{lbm}}\, J \frac{\text{molec.}}{\text{ft}^2\,\text{hr}} = m h_{fg}\, n \sqrt{\frac{kT}{2\pi m}} = \rho h_{fg} \sqrt{\frac{R^\circ T}{2\pi M}}$$

$$q_{max} = \frac{1}{26.8}(970.3)\sqrt{\frac{1545(672)}{6.28(18.02)}\,32.2}\;(3600) = \underline{\underline{7.08 \times 10^7 \;\frac{\text{Btu}}{\text{ft}^2\text{hr}}}}$$

Possibly the highest heat flux ever realized in a phase-change experiment was 55,000,000 $\frac{\text{Btu}}{\text{ft}^2\text{hr}}$ (by Gambill and Greene at ONRL in a special boiling configuration at a higher pressure than 1 atm.)

This result indicates that such heat transfer processes might start to be limited by molecular accomodation.

CHAPTER 3

3.1 Total number of possible microstates $= 6 \times 6 = 36$.

$\mathcal{P}(\text{microstate}) = \underline{\underline{\frac{1}{36}}}$. There are 3 ways to roll a 4:

so $\mathcal{P}(\text{macrostate}, 4) = \frac{3}{36} = \underline{\underline{\frac{1}{12}}}$

$$W(\text{macrostate}, 4) = \frac{\mathcal{P}(\text{macro}, 4)}{\mathcal{P}(\text{micro.})} = \begin{array}{c}\text{No. ways}\\ \text{to roll 4}\end{array} = \frac{1/12}{1/36} = \underline{\underline{3}}$$

If the dice are not loaded, all microstates will be equally probable and the principle of equal a' priori probabilities applies to them.

3.2 "A" knows what the card is so the thermodynamic probability associated with it has to be unity

$$S_A = k \ln W = k \ln 1 = \underline{\underline{0}}$$

"B" will probably assume the card to be from a standard 52 card playing deck. Then he might assume it to have 1/52 of the entropy of a 52 card deck. Under these assumptions,

$$W = N! \qquad \ln W = 52 \ln 52 - 52 = 52(3.95 - 1) = 206$$

so

$$S_B = (k \ln N!) \div 52 = \frac{1.38 \times 10^{-16} (206)}{52} = \underline{\underline{5.45 \times 10^{-16} \frac{\text{erg}}{^\circ K}}}$$

Of course "A" might have turned up a Joker or a Tarot card, in which case B's computation would be worthless.

3.3 a.) $W_{eq} = \frac{N!}{(N_{eq}!)^{N/N_{eq}}}$; $\underline{W_{ne} = \frac{N!}{(N_{eq}!)^{(N/N_{eq})-2}(N_{eq}-n)!(N_{eq}+n)!}}$

b.) $$\frac{W_{ne}}{W_{eq}} = \frac{(N_{eq}!)^2}{(N_{eq}-n)!\,(N_{eq}+n)!}$$

$$\ln\frac{W_{ne}}{W_{eq}} = 2\ln(N_{eq}!) - \ln(N_{eq}-n)! - \ln(N_{eq}+n)!$$

$$= -(N_{eq}-n)\ln\left(1-\frac{n}{N_{eq}}\right) - (N_{eq}+n)\ln\left(1+\frac{n}{N_{eq}}\right)$$

$$= -\left(N_{eq}-n\right)\left[-\frac{n}{N_{eq}} - \frac{1}{2}\left(\frac{n}{N_{eq}}\right)^2 - \frac{1}{3}\left(\frac{n}{N_{eq}}\right)^3 - \dots\right] - \left(N_{eq}+n\right)\left[\frac{n}{N_{eq}} - \frac{1}{2}\left(\frac{n}{N_{eq}}\right)^2 + \frac{1}{3}\left(\frac{n}{N_{eq}}\right)^3 - \dots\right]$$

$$= -N_{eq}\left(\frac{n}{N_{eq}}\right)^2\left[1 + \mathcal{O}\left(\frac{n}{N_e}\right)^2\right]$$

$$\underline{= -N_{eq}\left(\frac{n}{N_{eq}}\right)^2}$$

now $\frac{n}{N_{eq}} = .01$ and $N_{eq} = \frac{6.03\times10^{23}}{22.4\times10^{3}} = 2.69\times10^{19}$ particles

so $$\frac{W_{ne}}{W_{eq}} = e^{-0.01^2\times N_{eq}} = \underline{e^{-2.69\times10^{15}}}$$

(a number that is incomprehensibly small, such a fluctuation is thus impossible)

We would <u>expect</u> to find a deviation such that $W_{ne}/W_{eq} = 1/1000$, at least once in a Thousand pairs. Thus $\left.\frac{n}{N_{eq}}\right|_{max} = \sqrt{\frac{\ln(1000)}{2.69\times10^{19}}} = 5.07(10)^{-10}$

(a pretty unnoticable fluctuation)

C.) $$\Delta S = k\ln W_{ne} - k\ln W_{eq} = 1.38\times10^{-23}\ln e^{-2.69\times10^{15}}$$
$$= -1.38\times2.69\times10^{-8} = \underline{-3.71\times10^{-8}\,\text{Joule}/{}^\circ K}$$

3.4 $$Z = \sum e^{-\epsilon_i/kT} = \frac{1}{\Delta\tau}\iint_A \iint_{-\infty}^{\infty} \exp\left(-\frac{p_u^2+p_v^2}{2mkT}\right) dp_u\, dp_v\, dx\, dy$$

$$\underline{Z = \frac{A}{\Delta\tau}(2\pi m kT)}$$

Fundamental eq. $= F(T,A,N) = -NkT \ln Z = \underline{-NkT \ln \frac{2\pi A m kT}{\Delta\tau}}$

eqs. of state:

$$\underline{-S = \frac{\partial F}{\partial T} = -Nk\left[\ln \frac{2\pi A m kT}{\Delta\tau} + 1\right]}$$

$$\underline{-\text{"}p\text{"} = \frac{\partial F}{\partial A} = -\frac{NkT}{A}}$$

$$\underline{\mu = \frac{\partial F}{\partial N} = -kT \ln \frac{2\pi m A kT}{\Delta\tau}}$$

3.5 $$p = T \left.\frac{\partial S}{\partial V}\right|_{U,N} = T\frac{\partial}{\partial V}\left(kN\ln Z + \frac{U}{T}\right) = \underline{kTN \left.\frac{\partial \ln Z}{\partial V}\right|_{U,N}} \quad \text{Eq. (3.25)}$$

$-\frac{F}{T} = S - \frac{U}{T}$ so $\underline{F = -kTN \ln Z}$ Eq (3.24)

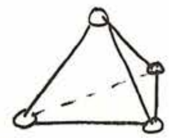
To get Eq. (3.23) cf. $\left.\frac{\partial F}{\partial T}\right|_{V,N} = -S$ with the derivative of Eq. (3.24)

$$-kN\ln Z - \frac{U}{T} = -kN\ln Z - kTN\left.\frac{\partial \ln Z}{\partial T}\right|_{V,N}$$

so $$\underline{U = kT^2 N \left.\frac{\partial \ln Z}{\partial T}\right|_{V,N}} \quad \text{Eq. (3.23)}$$

3.6 This is essentially a self-study exercise in which the fairly elementary student is asked to check his understanding of the steps which are laid out in Sec. 3.6.

3.7



The molecule has three excitable modes of translation and three excitable modes of rotation. It has six excitable modes of vibration.

$$D = 3 + 3 + 2 \times 6 = 18 \; ; \qquad c_v = \frac{D}{2} R^\circ = \underline{\underline{9 R^\circ}}$$

$$\gamma = \frac{D+2}{D} = \frac{10}{9} = \underline{\underline{1.1111}}$$

3.8 $$p = kTN_A \frac{\partial \ln Z}{\partial V} = R^\circ T \frac{\partial \ln (2\pi m k T)^{3/2} V/\Delta\tau}{\partial V} = \underline{\underline{\frac{R^\circ T}{V}}}$$

Chapter 4

4.1 Planck's radiation law, Eq.(4.34) $u_\lambda = \frac{8\pi h c_l}{\lambda^5[\exp(hc_l/\lambda kT)-1]}$

For $\frac{\lambda kT}{hc_l} \ll 1$, $\quad u_\lambda \approx \underline{\underline{\left(\frac{8\pi h c_l}{\lambda^5}\right) e^{-hc_l/\lambda kT}}}$

It is Wien's distribution (see Eq.(4.7)).

For $\frac{\lambda kT}{hc_l} \gg 1$, $\quad u_\lambda \approx \frac{8\pi h c_l}{\lambda^5[\cancel{1}+hc_l/\lambda kT+\cdots-\cancel{1}]} = \underline{\underline{\frac{8\pi kT}{\lambda^4}}}$

It is the Rayleigh-Jeans law (See Eq.(4.23)).

4.2 1.) $u_\lambda = \frac{8\pi h c_l}{\lambda^5[\exp(hc_l/\lambda kT)-1]}$ Eq.(4.34)

$$\frac{\partial u_\lambda}{\partial \lambda} = \left(-\frac{hc_l}{\lambda^2 kT} + \frac{5}{\lambda}\right)\left\{\lambda^5\left[\exp\left(\frac{hc_l}{\lambda kT}\right)-1\right]\right\}^{-1}$$

Since $\left.\frac{\partial u_\lambda}{\partial \lambda}\right|_{\lambda T = 0.2898\,\text{cm}^\circ\text{K}} = 0$ (see Eq.(4.8))

$$-\frac{hc_l}{\lambda^2 kT} + \frac{5}{\lambda} = 0$$

$$h = \frac{5kT\lambda}{c_l} = \frac{5(1.3805\times10^{-16})(0.2898)}{2.998\times10^{10}} = \underline{\underline{6.625\times10^{-27}}}\ \text{erg-sec}$$

2.) $\sigma T^4 = \frac{2\pi k^4 T^4}{c_l^2 h^3}\underbrace{\int_0^\infty \frac{x^3 e^{-x}}{1-e^{-x}}dx}$ Eq.(4.37)

$$\int_0^\infty x^3 e^{-x}\left[1+e^{-x}+e^{-2x}+\ldots\right]dx = \sum_{n=1}^\infty \int_0^\infty x^3 e^{-nx}dx$$

$$= \sum_{n=1}^\infty n^{-4}\Gamma(4)$$

$$= 6\left(\frac{\pi^4}{90}\right) \quad \text{See Eq.(4.38)}$$

Gamma fc. $\Gamma(s) = \int_0^\infty e^{-t} t^{s-1} dt$

$\Gamma(s) = (s-1)!$ $\quad s$ – positive integer

$$\sigma = \frac{2\pi^5 k^4}{15 c_l^2 h^3} = \frac{2\pi^5(1.3805\times10^{-16})^4}{15(2.998\times10^{10})^2(6.625\times10^{-27})^3} = \underline{\underline{5.6697\times10^{-5}}}\ \frac{\text{erg}}{\text{cm}^2\,\text{sec}\,^\circ\text{K}^4}$$

Eq.(4.39)

4.3 $$C_v = 3R^\circ \frac{x^2 e^x}{(e^x-1)^2} \qquad Eq. (4.41a)$$

$$x = h\nu/kT = \Theta/T$$

$$\lim_{T/\Theta\to\infty} (C_v) = \lim_{x\to 0} 3R^\circ \frac{x^2e^x}{(e^x-1)^2} = \underline{\underline{3R^\circ \lim_{x\to 0} \frac{x^2e^x}{(e^x-1)^2}}}$$

Apply L'Hospital's rule: (i.e. differentiating the denominator and numerator respectively w.r.to x)

$$\lim_{x\to 0} \frac{x^2e^x}{(e^x-1)^2} = \lim_{x\to 0} \frac{x^2\cancel{e^x}+2x\cancel{e^x}}{2(e^x-1)\cancel{e^x}} = \lim_{x\to 0} \frac{2x+2}{2e^x} = \underline{\underline{1}}$$

4.4 Einstein's specific heat law $C_v = 3R^\circ \frac{x^2e^x}{(e^x-1)^2}$ Eq.(4.41a)

a) Fourth postulate: $T\to 0$, $S\to$ constant or zero

thus $\Delta S \to 0 \quad C_v \equiv T\left(\frac{\partial S}{\partial T}\right)_v \to 0$

$T\to 0 \quad x = h\nu/kT \to \infty$

$$\lim_{x\to\infty} (C_v) = 3R^\circ \lim_{x\to\infty} \frac{x^2e^x}{(e^x-1)^2} \overset{\text{(see solution of Prob. 4.3)}}{=\!=} 3R^\circ \lim_{x\to\infty} \frac{2x+2}{2e^x}$$

$$= 3R^\circ \lim_{x\to\infty} \frac{2}{2e^x} = \underline{\underline{0}}$$

b) the classical specific heat law $C_v = 3R^\circ$ Eq.(4.40)

at large T $(x\to 0)$ $C_v = 3R^\circ \frac{x^2e^x}{(e^x-1)^2} \to 3R^\circ$

(see solution of Prob. 4.3)

4.5 $$\nabla^2 E_x = \frac{1}{c_\ell^2}\frac{\partial^2 E_x}{\partial t^2} \qquad Eq. (4.11)$$

$$E_x(0,y,z,t) = E_x(a,y,z,t) = 0$$
$$E_x(x,0,z,t) = E_x(x,b,z,t) = 0 \quad \text{From } Eq. (4.12)$$
$$E_x(x,y,0,t) = E_x(x,y,c,t) = 0$$

Let $E_x(x,y,z,t) = T(t)\,X(x)\,Y(y)\,Z(z)$ product solution

Eq.(4.11) becomes $\quad \dfrac{X''}{X} + \dfrac{Y''}{Y} + \dfrac{Z''}{Z} = \dfrac{1}{c_\ell^2}\dfrac{T''}{T} = -k^2$ eigenvalue

$T'' + k^2 c_\ell^2 T = 0 \qquad T = c_1 \sin k c_\ell t$ or $c_1 \cos k c_\ell t$

(since no initial conditions are given)

take $T = c_1 \sin k c_\ell t$ or in terms of frequency:

$$T = c_1 \sin 2\pi\nu t \qquad \nu = \left(\frac{k c_\ell}{2\pi}\right)$$

Since X''/X is fc. of x only, so are Y''/Y & Z''/Z,

$$\frac{X''}{X} + \frac{Y''}{Y} + \frac{Z''}{Z} = -k^2 = -(k_x^2 + k_y^2 + k_z^2)$$

$$X'' + k_x^2 X = 0, \quad Y'' + k_y^2 Y = 0, \quad Z'' + k_z^2 Z = 0$$

With boundary conditions given in Eq. (4.12), we have

$$X = c_2 \sin k_x x = c_2 \sin \frac{n_x \pi x}{a} \qquad k_x = \frac{n_x \pi}{a}$$

and so on for Y & Z

Eq.(4.13)

Therefore $\quad E_x = C \sin(2\pi\nu t)\sin\left(\dfrac{n_x \pi x}{a}\right)\sin\left(\dfrac{n_y \pi y}{b}\right)\sin\left(\dfrac{n_z \pi z}{c}\right)$

where $\quad \left(\dfrac{\nu}{c_\ell}\right)^2 = \left(\dfrac{n_x}{2a}\right)^2 + \left(\dfrac{n_y}{2b}\right)^2 + \left(\dfrac{n_z}{2c}\right)^2 \quad$ [see Eq. (4.18)]

4.6 Solution of 2-dim. Maxwell's equations: See solution of Prob. 4.5.

$$\sigma_2 = \frac{2k^3}{c_\ell h^2}\int_0^\infty \frac{x^2}{e^x - 1}\,dx$$

From Appendix E: $\displaystyle\int_0^\infty \frac{x^2}{e^x-1}\,dx = 2\zeta(3) = 2.404114$ (See also Solution of Prob.(4.3))

$$\sigma_2 = \frac{2(1.3805\times10^{-16})^3(2.404114)}{(2.998\times10^{10})(6.625\times10^{-27})^2} = \underline{\underline{9.97\times10^{-5}}}\ \frac{\text{erg}}{\text{cm sec °K}^3}$$

4.7 <u>Hg</u>. At 1 atm, the boiling point of Hg is about 350°C, and Hg at 1 atm and 200°C is thus in the liquid state. Since the intermolecular potential (U) is complicated, a calculation of $\lambda = \frac{h}{p} = \frac{h}{\sqrt{2mE}}$ with $E = \frac{3}{2}kT + U$ is not easy. Since the pressure is not stated, however, we can still have gaseous state of Hg at 200°C and at low pressures (in this case $p < 0.38$ psia), and the Hg-atoms can be assumed as independent, and $U = 0$. Thus

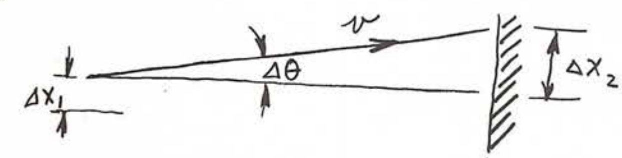
$$\lambda = \frac{h}{\sqrt{3mkT}} = \frac{6.624\times10^{-27}}{\left[3\times\frac{200}{6.02\times10^{23}}(1.38\times10^{-16})\,473\right]^{1/2}} = \underline{\underline{8.20\times10^{-10}\text{ cm}}}$$

λ_{Hg} is about two orders of magnitude less than the size of Hg.

<u>Bullet</u> $\lambda = \frac{h}{mv} = \frac{6.624\times10^{-27}}{\frac{1}{16}\times454\times10^{5}} = \underline{\underline{2.33\times10^{-33}\text{ cm}}}$

λ_{bullet} is very small because of the large mass

4.8



Eq. (4.62) $\Delta p_x \Delta x \geq \frac{\hbar}{2}$

$$\Delta p_{x_1}\Delta x_1 = \Delta(m v_{x_1})\Delta x_1 = m\Delta v_{x_1}\Delta x_1 = m\left(\frac{\Delta x_1}{t}\right)\Delta x_1 \quad (\because v = \text{const.})$$

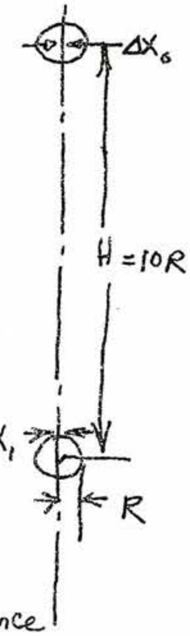
Since $\Delta x_2 = (\Delta v_{x_1})t = \frac{\Delta x_1}{t}t = \Delta x_1$

$$\Delta x = \Delta x_1 + \Delta x_2 = 2\Delta x_1 = 2\sqrt{\frac{\hbar t}{2m}} = 2\left[\frac{1.054\times10^{-27}\times 0.5 \;\; 0.2222}{2\times \frac{454}{16} \;\; 20}\right]^{\frac{1}{2}}$$

$$= \underline{\underline{\cancel{6.12}\;4.84\times10^{-15}\text{ cm}}}$$

4.9

$$\Delta X_1 = \Delta X_0 + \Delta v_x \sqrt{\frac{2H}{g}}$$



According to uncertainty relation

$$\Delta X_0\, m \Delta v_x = \frac{h}{4\pi}$$

$$\Delta X_1 = \Delta X_0 + \sqrt{\frac{2H}{g}}\, \frac{h}{4\pi m \Delta X_0}$$

$$\frac{d\Delta x_1}{d\Delta X_0} = 0 \qquad \Delta X_0 = \sqrt{\frac{h}{4\pi m}\sqrt{\frac{2H}{g}}}$$

$$\Delta V_x = \frac{h}{4m\pi \Delta X_0} = \sqrt{\frac{h}{4\pi m}\sqrt{\frac{g}{2H}}}$$

$$\Delta X_1 = \Delta X_0 + \Delta v_x \sqrt{\frac{2H}{g}} = 2\Delta X_0$$

let θ_1 is the angle with the vertical after the 1st bounce

$$\epsilon_1 = \sin\theta_1 = 2\left[\frac{\Delta X_0 + \Delta V_x\sqrt{\frac{2H}{g}}}{R} + \cancel{\frac{\Delta v_x \sqrt{\frac{2H}{g}}}{H}}\right]$$

$$= \frac{2\Delta X_1}{R} = \frac{4\Delta X_0}{R}$$

negligible, one order-of-magnitude less than the 2nd term

$$\Delta X_2 = \Delta X_1 + 2Vt\,\epsilon_1 = \Delta X_1 + 2\sqrt{2gH}\sqrt{\frac{2H}{g}}\,\frac{2\Delta X_1}{R} = 81\,\Delta X_1$$

$$\Delta X_3 = 81\,\Delta X_2,\ \cdots,\quad \Delta X_n = (81)^{n-1}\Delta X_1$$

the final bounce is when $\Delta X_n = R$, or $(81)^{n-1}\Delta X_1 = R$

$$(81)^{n-1}\, 2\sqrt{\frac{h}{4\pi m}\sqrt{\frac{2H}{g}}} = R$$

For a given R, solve the value of n and the closest but smaller integer is the number of bounces.

Chapter 5

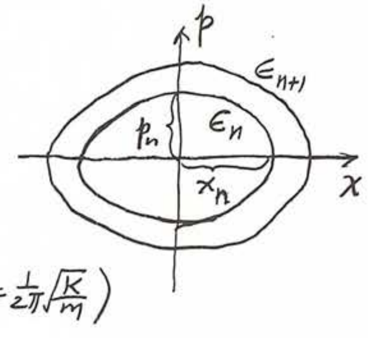
5.1 3-dim. case $\quad -\frac{\hbar^2}{2m}\nabla^2\psi = \epsilon\psi$

let $\psi = X(x)\,Y(y)\,Z(z)$

$$\frac{X''}{X} + \frac{Y''}{Y} + \frac{Z''}{Z} = -\frac{2m\epsilon}{\hbar^2} = -\frac{2m}{\hbar^2}(\epsilon_x+\epsilon_y+\epsilon_z)$$

Solution for ψ [Eq. (5.6)] and relation for ϵ [Eq. (5.7)] can be obtained by following identical steps in the solution of Prob 4.5.

5.2 Classical: $\quad \epsilon_n = \frac{p^2}{2m} + \frac{Kx^2}{2}$
(an ellipse)



Quantum: $\quad \epsilon_n = (n+\frac{1}{2})h\nu \quad \left(\nu = \frac{1}{2\pi}\sqrt{\frac{K}{m}}\right)$

Area enclosed by ϵ_n-ellipse:

$$A_n = \pi p_n x_n = \pi(\sqrt{2m\epsilon})\left(\sqrt{\frac{2\epsilon}{K}}\right) = \epsilon\pi\sqrt{\frac{4m}{K}} = \frac{\epsilon}{\nu}$$

The cell-volume in 2-dim τ-space $= \Delta A = A_{n+1} - A_n = \frac{\Delta\epsilon}{\nu} = \frac{h\nu}{\nu} = \underline{\underline{h}}$.
Thus the general assertion following eq. (5.35a) is upheld.

5.3 From Eq. (4.68) $\quad \frac{\partial^2\Psi}{\partial x^2} = \frac{2m}{i\hbar}\frac{\partial\Psi}{\partial t} \quad (U=0)$

Note: Solution of this equation (e.g. by separation-of-variable method) will be of the same form as obtained from the classical wave equation because of the imaginary coefficient (see comments on top of p.106).

5.4 $\quad U = \frac{1}{2}kx^2 + U_0$

From Eq. (5.9) $\quad -\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} + \left(\frac{kx^2}{2} + U_0 - \epsilon\right)\psi = 0$.

Since $(U_0 - \epsilon)$ is a constant, the solution is, the same as for the linear harmonic oscillator: $\underline{\underline{\epsilon = (n+\frac{1}{2})h\nu + U_0}}$

(The same result can also be obtained by solving the boundary value problem, but the labor is unnecessary.)

5.5 $\quad U(x<0) = \infty \;,\; U(x \geq 0) = Ax^2$

$$\begin{cases} -\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} + (Ax^2 - \epsilon)\psi = 0 & (x \geq 0) \quad (A) \\ -\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} + (U_0 - \epsilon)\psi = 0 & (U_0 \to \infty,\; x<0) \quad (B) \end{cases}$$

To determine the boundary conditions:

$\psi = 0$ at $x \to \infty$ (because of the restoring force $F = -\frac{dU}{dx} = -2Ax$, $x \to \infty$, $F \to \infty$, the probability of having any particle at $x \to \infty$ is zero)

$\psi = 0$ at $x = 0$ (because $U_0 \to \infty$, $x<0$)

Mathematically, $\psi = 0$ at $x \to \infty$ is required in (A) in order to have a non-singular 2nd term, while $\psi = 0$ at $x = 0$ may also be obtained by matching (A) and (B) solutions at $x = 0$.

Let $\psi(\xi) = Q(\xi)e^{-\xi^2/2}$, $\quad \xi = \left(\frac{2\pi}{h}\right)^{1/2}(2mA)^{1/4}x$

(this satisfies the condition $\psi \to 0$ at $x \to \infty$)

we have
$$\frac{d^2Q}{d\xi^2} - 2\xi\frac{dQ}{d\xi} + mQ = 0 \qquad (\xi \geq 0)$$
$$m = \varepsilon\frac{4\pi}{h}\left(\frac{m}{2A}\right)^{1/2} - 1$$

In order to satisfy $\psi \to 0$ at $x \to 0$: $\quad Q = AH_{2n+1}(\xi)$

thus $\quad \psi(\xi) = \underline{\underline{AH_{2n+1}(\xi)e^{-\xi^2/2}}}$

$$m = 2(2n+1) \Rightarrow \quad \underline{\underline{\epsilon = \frac{h}{\pi}\left(\frac{2A}{m}\right)^{1/2}\left(n + \frac{3}{4}\right)}}$$

5.6 Solution of Eq. (5.9a) : $Q(\xi) = H_n(\xi) = H_n(\alpha^{\frac{1}{2}} x)$

$$\psi = Q(\xi) e^{-\xi^2/2} = H_n(\alpha^{\frac{1}{2}} x) e^{-\alpha x^2/2}$$

To normalize ψ, i.e. to satify $\int_{-\infty}^{\infty} \psi_n \psi_n \, dx = 1$ [see Eq. (4.69)]

Since $$\int_{-\infty}^{\infty} e^{-\alpha x^2} H_n(\alpha^{\frac{1}{2}} x) H_m(\alpha^{\frac{1}{2}} x) \, d(\alpha^{\frac{1}{2}} x) = 2^n n! \, \pi^{1/2} \delta_{nm}$$

(orthogonal relation, see, for instance, Margenau and Murphy, The Mathematics of Physics and Chemistry, 2nd Ed., p. 124, McGraw-Hill, 1956)

$$\psi_n(x) = \left(\sqrt{\frac{\alpha}{\pi}} \frac{1}{2^n n!} \right)^{1/2} H_n(\alpha^{\frac{1}{2}} x) \, e^{-\alpha x^2/2}$$

ϵ_n-expression [Eq. (5.10a) or (5.10b)] can be obtained from Eq. (5.10) and the definitions of β and α.

5.7 The orthogonal relation for P_ℓ^m is

$$\int_{-1}^{1} P_\ell^m(\xi) \, P_n^m(\xi) \, d\xi = \left(\frac{2}{2\ell+1} \right) \frac{(\ell+m)!}{(\ell-m)!} \delta_{\ell n}$$

see, for instance, Margenau & Murphy, (cited above) p. 109.

Since $\psi(\theta, \phi) = P(\theta) \Phi(\phi) = P_\ell^m(\theta) e^{im\phi}$, to normalize ψ requires

$$c^2 \int_\theta \int_\phi [P_\ell^m(\theta)]^2 e^{i2m\phi} \sin\theta \, d\theta \, d\phi = 1 \qquad c: \text{constant}$$

Or $$c^2 \int_0^\pi [P_\ell^m(\theta)]^2 \sin\theta \, d\theta \int_0^{2\pi} e^{i2m\phi} \, d\phi = 1$$

$$c^2 \left[\left(\frac{2}{2\ell+1} \right) \frac{(\ell+m)!}{(\ell-m)!} \right] (2\pi) = 1$$

Thus $$\psi_{\text{normalized}} = \frac{1}{\sqrt{2\pi}} \left[\frac{(2\ell+1)(\ell-m)!}{2(\ell+m)!} \right] P_\ell^m(\cos\theta) \, e^{im\phi}$$

This is Eq. (5.15).

5.8 $\psi(\theta,\phi,r) = Y(\theta,\phi)R(r)$

$$Y(\theta,\phi) = \frac{1}{\sqrt{2\pi}}\left[\frac{(2l+1)(l-m)!}{2(m+l)!}\right]^{1/2} P_l^m(\cos\theta)e^{im\phi}$$

(see Eq. (5.15) and solution of Prob. 5.7)

$R(r)$ satisfies $\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) + \frac{2m_e}{\hbar^2}\left[\epsilon + \frac{C_1}{r} - \frac{l(l+1)\hbar^2}{2m_e r^2}\right]R = 0$

(Details of solution can be found, for instance, in Schiff, Quantum Mechanics, McGraw-Hill, 1955, §16)

Let $W = \alpha r$, $\alpha^2 = \frac{8m_e\epsilon}{\hbar^2}$, $n = \frac{C_1}{\hbar}\left(\frac{m_e}{2\epsilon}\right)^{1/2}$

We have $\frac{1}{W^2}\frac{d}{dW}\left(W^2\frac{dR}{dW}\right) + \left(\frac{n}{W} - \frac{1}{4} - \frac{l(l+1)}{W^2}\right)R = 0$

With $R(W) = W^l e^{-\frac{1}{2}W} L(W)$, there results

$$WL'' + [2(l+1) - W]L' + (n-l-1)L = 0$$

which is of the form of the associated Laguerre equation

$$WL_q^{p\,\prime\prime} + (p+1-W)L_q^{p\,\prime} + (q-p)L_q^p = 0$$

By comparison: $p = 2l+1$, $q = n+l$

The solution $L_q^p(W)$ is given by Eq. (5.18).

The normalization integral is

$$\int_0^\infty \left[W^l e^{-W/2} L_{n+l}^{2l+1}(W)\right]^2 W^2 dW = \frac{2n[(n+l)!]^3}{(n-l-1)!}$$

The normalized $R_n^l(r)$ is thus

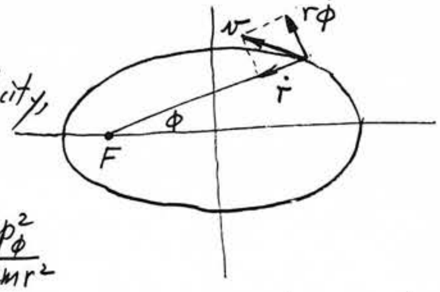
$$R_n^l(r) = -\left[\left(\frac{2}{na_0}\right)^3 \frac{(n-l-1)!}{2n[(n+l)!]^3}\right]^{1/2} \exp\left(-\frac{W}{2}\right) W^l L_{n+l}^{2l+1}(W)$$

$$\left(a_0 \equiv \frac{\hbar^2}{m_e C_1}\right)$$

and

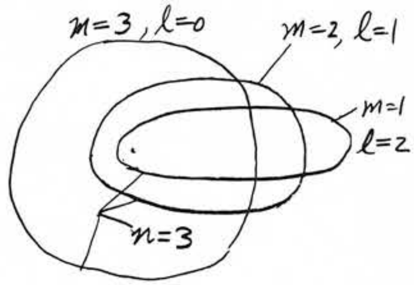
$$\psi(\theta,\phi,r) = Y_l^m(\theta,\phi)R_n^l(r)$$

5.9 In an elliptic orbit, there will be two components of velocity, and the kinetic energy KE can be written as



$$KE = \frac{p_r^2}{2m} + \frac{p_\phi^2}{2mr^2}$$

Each component will be characterized by a quantum number, say m and ℓ. The quantum number for the total energy of motion turns out to be $n = m + \ell$. For one n there could be several orbits, or in other words, for one line in the one-electron atom case [see Eq. (5.21b)], there could exist several lines in the fine structure.



5.10 $\epsilon = \frac{1}{2I}\left(p_\theta^2 + \frac{p_\phi^2}{\sin^2\theta}\right)$ Compare with Eq. (5.38)

$$d\tau = dp_\theta\, dp_\phi\, (\sin\theta\, d\theta)\, d\phi$$

$$Z_r = \frac{1}{h^2}\iint_{-\infty}^{\infty}\int_0^{\pi}\int_0^{2\pi} \exp\left[-\epsilon(\theta,\phi)/kT\right] dp_\theta\, dp_\phi\, (\sin\theta\, d\theta)\, d\phi = \underline{\underline{\frac{8\pi^2 IkT}{h^2}}}$$

5.11 $\epsilon = \frac{h^2}{8mV^{2/3}}(n_x^2 + n_y^2 + n_z^2) = \frac{h^2}{8mV^{2/3}}\, n^2$

Under normal conditions, most translational states are characterized by large n. The change in n can be treated as continuous. The number of quantum states corresponding to n is thus the spherical shell volume from n to $n+dn$: $g_n \Delta n = \frac{1}{8}(4\pi n^2 dn)$ or $\left(\frac{4\pi mV}{h^3}\right)(2m\epsilon)^{1/2} d\epsilon$

$$Z_t = \sum g_n e^{-\epsilon_n/kT} = \int e^{-\epsilon/kT}\left(\frac{4\pi mV}{h^3}\right)(2m\epsilon)^{1/2} d\epsilon = \underline{\underline{\frac{V}{h^3}(2\pi mkT)^{3/2}}}$$

5.12 From Eq. (5.28) $Z_t = \frac{V}{h^3}(2\pi m k T)^{3/2}$ (see, also, solution of Prob. 5.11)

$$Z_t = Z_x \cdot Z_y \cdot Z_z \qquad Z_x = Z_y = Z_z = \frac{V^{1/3}}{h}(2\pi m k T)^{1/2}$$

From Eqs. (3.12) and (5.25) $\frac{N_i}{N} = \frac{n_i}{n} = \frac{g_i}{Z} e^{-\epsilon_i/kT}$

(n & n_i are number densities)

1) Consider the 3-quantum number case with n_x, n_y, n_z

$$g_x = 1, \quad \epsilon_x = \frac{h^2 n_x^2}{8 m V^{2/3}} = \frac{1}{2} m v_x^2 \quad \text{or} \quad n_x = \frac{2 m V^{1/3}}{h} v_x$$

$$1 = \int_0^\infty \frac{g_i}{Z_x} e^{-\epsilon_i/kT} dn_x = \int_{-\infty} \frac{1}{n} f(v_x)\, dv_x = \int_0 \frac{2}{n} f(v_x) dv_x$$

$$f(v_x) = \frac{n}{\cancel{2}} \left(\frac{\cancel{2} m \cancel{V^{1/3}}}{\cancel{h}}\right) \frac{\cancel{h}}{\cancel{V^{1/3}}(2\pi m k T)^{1/2}} e^{-m v_x^2/2kT}$$

$$f(v_x) = n \left(\frac{m}{2\pi k T}\right)^{1/2} e^{-m v_x^2/2kT}$$

$$f(v_x, v_y, v_z) = n \left(\frac{m}{2\pi k T}\right)^{3/2} e^{-m(v_x^2 + v_y^2 + v_z^2)/2kT} \qquad \text{see Eq. (2.43)}$$

2) Consider the one-quantum-number case with n (see solution of Prob. 5.11)

$$1 = \int_0^\infty \frac{g}{Z} e^{-\epsilon/kT} dn = \int_0 \frac{1}{n} f(v)\, dv$$

$$g\,dn = \frac{4\pi m V}{h^3}(2m\epsilon)^{1/2} d\epsilon = \left(\frac{4\pi m V}{h^3} m v\right) m v\, dv$$

$$\frac{4\pi m \cancel{V} (mv)^2}{\cancel{h^3} \frac{\cancel{V}}{\cancel{h^3}}(2\pi m k T)^{3/2}} = \frac{1}{n} f(v)$$

$$f(v) = \left[4\pi \left(\frac{m}{2\pi k T}\right)^{3/2}\right] n v^2 e^{-mc^2/2kT} \qquad \text{see Eq. (2.46)}$$

5.13

$$Z_z = \left(\frac{1}{h}\right)^3 \int \exp\left[-\frac{p_x^2 + p_y^2 + p_z^2}{2mkT} - \frac{mgz}{kT}\right] dp_x dp_y dp_z\, dx\, dy\, dz$$

$$= \left(\frac{2\pi m k T}{h^2}\right)^{3/2} \iiint_{x\,y\,\Delta z} e^{-mgz/kT} dx dy dz = \left(\frac{2\pi m k T}{h^2}\right)^{3/2} V e^{-mgz/kT}$$

Note the difference of Z_z and Z in Ex. 3.2 where the integration is from 0 to z, while Z_z is based on a layer (Δz) at z and $Z_z = Z_z(T, V, N_z)$

$$p_z = N_z kT\left(\frac{\partial \ln Z_z}{\partial V}\right)_{T,N_z} = \frac{N_z kT}{V} \quad \left(\Rightarrow \frac{N_0 kT}{V} e^{-\frac{mgz}{kT}} = p_0 e^{-\frac{mgz}{kT}}\right)$$

Since N_z's at different z's are different, there is no way to obtain the N_z-distribution in the formulation presented so far. This must be obtained through the formulation of the grand canonical ensemble (Chapter 8).

5.14
$$\epsilon = \frac{p^2}{2m} + \frac{kx^2}{2}$$

$$Z_v = \frac{1}{h}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} \exp\left[-\left(\frac{p^2}{2m} + \frac{kx^2}{2}\right)/kT\right] dp\, dx = \frac{kT\, 2\pi}{h}\sqrt{\frac{m}{k}} = \underline{\underline{\frac{kT}{h\nu}}}$$

5.15
$$U(r) = -\int F\, dr = +\tfrac{1}{2} m\omega^2 r^2 \quad (0 < r < R)$$

The rigorous approach would be to solve the Schrödinger equation with given $U(r)$ and boundary conditions. However, the classical approach is much simpler and should give a good approximation at moderate temperatures.

$$\epsilon = \frac{1}{2m}\left(p_x^2 + p_y^2 + p_z^2\right) + \tfrac{1}{2} m\omega^2 r^2$$

$$Z = \frac{V}{h^3}\iiint_{-\infty}^{\infty} \exp\left[-(p_x^2+p_y^2+p_z^2)/2mkT\right] dp_x\, dp_y\, dp_z \, \frac{V}{h} \int_0^L\int_0^R 2\pi r \exp\left(\frac{-m\omega^2 r^2}{2kT}\right) dr\, dz$$

$$= \frac{1}{h^3}(2\pi mkT)^{3/2}\left(\frac{2\pi L kT}{m\omega^2}\right)\left(e^{-m\omega^2R^2/2kT} - 1\right)$$

$$U = NkT^2 \frac{\partial \ln Z}{\partial T} = \frac{5}{2}NkT \mp \frac{Nm\omega^2 R^2}{2\left[\exp(\mp m\omega^2R^2/2kT) - 1\right]}$$

5.16
$$\epsilon = \frac{p^2}{2m} + cx^2 - gx^3 - fx^4$$

$$Z = \frac{1}{h}\int e^{-\epsilon/kT} dp\, dx = \frac{1}{h}\int_{-\infty}^{\infty} e^{-p^2/2mkT} dp \int_{-\infty}^{\infty} e^{-(cx^2 - gx^3 - fx^4)/kT} dx$$

$$= \left(\frac{2\pi mkT}{h^2}\right)^{1/2}\int_{-\infty}^{\infty} e^{-cx^2/kT}\left(1 + \frac{gx^3}{kT} + \frac{fx^4}{kT} + \frac{g^2x^6}{2k^2T^2} + \cdots\right) dx$$

$$= \left(\frac{2\pi mkT}{h^2}\right)^{1/2}\left(\frac{\pi kT}{2c}\right)^{1/2}\left(1 + \frac{3}{4}\frac{fkT}{c^2} + \frac{15}{16}\frac{g^2kT}{c^3} + \cdots\right)$$

5.16 (Continued)

Since $\ln(1+x) \approx x$ for $x \ll 1$

$$\ln Z = \ln\left(\frac{2\pi m k T}{h^2}\right)^{1/2}\left(\frac{\pi k T}{2c}\right)^{1/2} + \frac{3}{4}\frac{f k T}{c^2} + \frac{15}{16}\frac{g^2 k T}{c^3}$$

$$c_v = \left(\frac{\partial U}{\partial T}\right)_V = \frac{\partial}{\partial T}\left(N k^2 T\, \frac{\partial \ln Z}{\partial T}\right) \qquad N = 1$$

$$= k\left[1 + \left(\frac{3f}{2c^2} + \frac{15 g^2}{8c^3}\right) kT\right]$$

This solution depends upon the fact that f and g are small. They have to be small since we are only dealing with corrections for a basically harmonic motion.

Chapter 6

6.1 <u>Eq. (6.5a)</u> $$d\ln W_B = d\ln\left\{N!\prod \frac{g_i^{N_i}}{N_i!}\right\} = 0$$

$$0 = d\ln N! + \sum d\left[N_i \ln g_i - N_i \ln N_i + N_i\right]$$

$$= \sum\left[\ln g_i - \ln N_i - 1 + 1\right]dN_i = \sum \ln(g_i/N_i)\,dN_i$$

add to this the constraints $\sum \alpha\, dN_i = 0$; $\sum \beta\epsilon_i\, dN_i = 0$

$$\sum\left[\ln(g_i/N_i) - (\alpha + \beta\epsilon_i)\right]dN_i = 0$$

so $$N_i = \frac{g_i}{e^{\alpha}e^{\beta\epsilon_i}} \quad \text{or} \quad \frac{N_i}{\sum N_i} = \underline{\frac{N_i}{N} = \frac{g_i e^{-\beta\epsilon_i}}{\sum g_i e^{-\beta\epsilon_i}} = \frac{g_i e^{-\beta\epsilon_i}}{Z}}$$

<u>Eq. (6.6)</u> $$d\ln W_{BE} = \sum d\ln\left[\frac{(g_i + N_i - 1)!}{(g_i - 1)!\,N_i!}\right] = 0$$

$$0 = \sum d\left[(g_i + N_i - 1)\ln(g_i + N_i - 1) - g_i - N_i + 1 - \ln(g_i - 1)! - N_i \ln N_i + N_i\right]$$

$$0 = \sum\left[1 + \ln(g_i + N_i - 1) - 1 - \ln N_i - 1 + 1\right]dN_i$$

add the same constraints and simplify

$$0 = \sum\left[(\alpha + \beta\epsilon_i) + \ln\left(\frac{g_i}{N_i} + 1 - \underbrace{\frac{1}{N_i}}_{\text{neglect, } \ll 1}\right)\right]dN_i$$

so $$\underline{N_i = \frac{g_i}{e^{+\alpha}e^{+\beta\epsilon_i} - 1}}$$

<u>Eq. (6.7)</u> $$d\ln W_{FD} = \sum d\ln\left[\frac{g_i!}{N_i!\,(g_i - N_i)!}\right] = 0$$

$$0 = \sum -d\left[N_i \ln N_i - N_i + (g_i - N_i)\ln(g_i - N_i) - (g_i - N_i) - \ln g_i!\right]$$

differentiate and add the same constraints

$$0 = \sum\left[\alpha + \beta\epsilon_i - \ln N_i + \ln(g_i - N_i)\right]dN_i$$

so $$\underline{N_i = \frac{g_i}{e^{\alpha}e^{\beta\epsilon_i} + 1}}$$

6.2 $d \ln \frac{W_B}{N!} = d \ln \prod \frac{g_i^{N_i}}{N_i!} = \sum d(N_i \ln g_i - N_i \ln N_i + N_i) = 0$

but from this point on, the derivation is exactly the same as the derivation of Eq. (6.5a) in Problem 6.1.

6.3 In accordance with Eq. (6.5a)

$$\frac{N_i}{N} = \frac{A t_i^2 e^{-\beta t_i^2}}{\sum A t_i^2 e^{-\beta t_i^2}} \quad \text{where} \quad \sum N_i = N, \quad \sum t_i^2 N_i = t_{rms}^2 N$$

The partition function can be evaluated as

$$Z \simeq \frac{A}{\Delta t}\int_0^\infty t^2 e^{-\beta t^2} dt = \underline{\frac{A}{\Delta t}\frac{\sqrt{\pi}}{4\beta^{3/2}}}$$

Thus the second constraint can be evaluated as

$$\sum \frac{1}{t_{rms}^2} t_i^2 \frac{N_i}{N} = 1 = \frac{1}{\Delta t\, t_{rms}^2}\int_0^\infty \frac{\Delta t}{A}\frac{4\beta^{3/2}}{\sqrt{\pi}} t^2 \left(A t^2 e^{-\beta t^2}\right) dt$$

or

$$t_{rms}^2 \frac{\sqrt{\pi}}{4\beta^{3/2}} = \int_0^\infty t^4 e^{-\beta t^2} dt = \frac{\Gamma(5/2)}{2\beta^{5/2}} \quad ; \quad \underline{\beta = \frac{3}{2} t_{rms}^{-2}}$$

Thus $$\frac{N_i}{N} = \frac{N_i}{e^{\alpha} Z} = \frac{e^{\alpha}}{e^{\alpha}}\frac{\Delta t}{A}\frac{4\beta^{3/2}}{\sqrt{\pi}} A t_i^2 e^{-\beta t_i^2}$$

or with the help of Eq. (2.11)

$$\underline{F(t) = \lim_{\Delta t \to 0}\left(\frac{N_i}{N \Delta t}\right) = \sqrt{\frac{54}{\pi}}\frac{1}{t_{rms}}\left(\frac{t}{t_{rms}}\right)^2 \exp\left(-\frac{3}{2}\left[\frac{t}{t_{rms}}\right]^2\right)}$$

This result is applied and discussed fully in the <u>Jour. of Geophysical Research</u>, vol. <u>69</u>, no. 24, (1964), p. 5231.

6.4 (cf. with Problem 6.3) $\frac{N_i}{N} = \frac{A t_i^{n-1} \exp(-B t_i^{\beta})}{\sum A t_i^{n-1} \exp(-B t_i^{\beta})}$

where B is what we formerly called the lagrangian multiplier, β. The constraints are

$$\sum N_i = N \quad \text{and} \quad \sum N_i t_i^{\beta} = N t_{rm\beta}^{\beta}$$

Now $$Z \simeq \frac{A}{\Delta t}\int_0^{\infty} t^{n-1} e^{-Bt^{\beta}} dt = \frac{A}{\Delta t}\frac{\Gamma(\frac{n}{\beta})}{\beta \cdot B^{n/\beta}}$$

and
$$\sum \frac{1}{t_{rm\beta}^{\beta}} t_i^{\beta} \frac{N_i}{N} = 1 \simeq \frac{1}{\Delta t}\int_0^{\infty} \frac{\Delta t\, \beta B^{n/\beta}}{A\,\Gamma(\frac{n}{\beta})\, t_{rm\beta}^{\beta}} t^{\beta+n-1} e^{-Bt^{\beta}} dt$$

or
$$\frac{\Gamma(\frac{n}{\beta})\, t_{rm\beta}^{\beta}}{\beta B^{n/\beta}} = \frac{\Gamma(\frac{\beta+n}{\beta})}{\beta B^{(\beta+n)/\beta}} \quad ; \quad \underline{B = \frac{n/\beta}{t_{rm\beta}^{\beta}}}$$

Thus
$$\frac{N_i}{N} = \Delta t\, \beta \frac{t_i^{n-1} \exp\left(-\frac{n}{\beta}\left[\frac{t_i}{t_{rm\beta}}\right]^{\beta}\right)}{\Gamma(\frac{n}{\beta})\, (\frac{n}{\beta})^{n/\beta}\, t_{rm\beta}^{n}}$$

and
$$\underline{F(t) = \frac{\beta}{t_{rm\beta}\, (\frac{n}{\beta})^{n/\beta}\, \Gamma(\frac{n}{\beta})}\left(\frac{t}{t_{rm\beta}}\right)^{n-1} \exp\left(-\frac{n}{\beta}\left[\frac{t}{t_{rm\beta}}\right]^{\beta}\right)}$$

This result and its many ramifications are treated in Quart. App. Math, vol. 25, no. 3, (1967), p. 330.

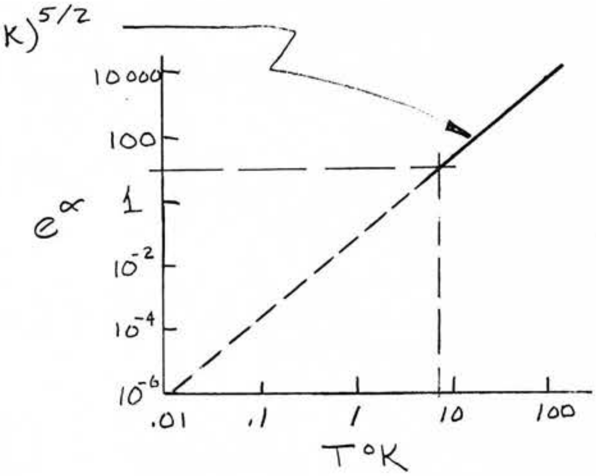
6.5 $$e^{\alpha} = \left[\frac{2\pi m kT}{h^2}\right]^{3/2} \frac{V}{N} = \left[\frac{6.28(M/N_A)kT}{h^2}\right]^{3/2} \frac{kT}{p}$$

let us take $p = 1\,\text{atm} = 1.013 \times 10^6\ \text{dyne/cm}^2$, and note that the $1\ \text{cm}^3$ specification is irrelevant without knowledge of N. Then

6.5 cont'd.

$$e^{\alpha} = \left[\frac{6.28\,(2/6.02\times10^{23})\,1.38\times10^{-16}}{(6.6256)^2\times10^{-54}}\right]\frac{1.38\times10^{-16}}{1.013\times10^{6}}\; T^{5/2}$$

$$e^{\alpha} = 0.070\,(T\,°K)^{5/2}$$



we can call

$e^{\alpha} \gg 1$ (say ≥ 10)

for $\underline{\underline{T > 7.3\,°K}}$

Note that the line is dotted for T below this limit because our equation is restricted to the range $e^{\alpha} \gg 1$.

6.6 By combining Eq. (6.11) with Example 5.4, we get

$$e^{\alpha} \simeq \frac{V}{\Lambda^3 N} = \frac{8Z}{n^3}\,\frac{V}{\lambda^3 N}$$ for particles to act as boltzons.

but, using Eq. (5.28) we find

$$e^{\alpha} \simeq \left(2\pi\,\frac{T}{n^2\Theta_t}\right)^{3/2}\frac{V}{\lambda^3 N}$$

Now, going to Eq. (5.27) we see that only quantum numbers for which $T/(n^2\Theta_t) \gtrsim 1/3$ will contribute. (remember that T/Θ_t and n^2 are both immense).

Thus $\underline{e^{\alpha} \simeq \left(\frac{2\pi}{3}\right)^{3/2}\frac{V}{\lambda^3 N}}$ when molecules can 1st be treated as boltzons.

6.6 cont'd

$$\left(\frac{2\pi}{3}\right)^{3/2} \frac{V}{\lambda^3 N} \simeq \frac{V}{\lambda^3 N} = \frac{\text{volume of space available to molecules}}{\text{volume over which all molecules are effectively smeared.}}$$

The implication of the result is that, since $e^{\alpha} \gg 1$, then $V/\lambda^3 N \gg 1$. Thus, for molecules to be treated as Boltzon's, the volume over which they circulate must be substantially greater than the volume occupied by their de Broglie waves. (This would not be the case at low temperatures or energy levels.)

6.7 From the second and third parts of the solution of Problem 6.1 we learn that

$$d \ln W_{BE \text{ or } FD} = \sum \ln \frac{g_i \pm N_i}{N_i} \, dN_i$$

but $g_i/N_i = e^{\alpha} e^{\beta \epsilon_i} \mp 1$ so

$$\underline{d \ln W_{BE \text{ or } FD} = \alpha \sum dN_i + \beta \sum \epsilon_i dN_i}$$

6.8 If we note that g_i & $N_i \gg 1$, then

$$\ln W_{BE} = \sum \left\{ (g_i + N_i) \ln (g_i + N_i) - (g_i + N_i) - g_i \ln g_i + g_i - N_i \ln N_i + N_i \right\}$$

$$\ln W_{FD} = \sum \left\{ -N_i \ln N_i + N_i - (g_i - N_i) \ln (g_i - N_i) + (g_i - N_i) + g_i \ln g_i - g_i \right\}$$

Both of these simplify to

$$\ln W_{BE \text{ or } FD} = \sum \left\{ (N_i \pm g_i) \ln \left(\frac{g_i}{N_i} \pm 1 \right) \mp g_i \ln \frac{g_i}{N_i} \right\}$$

substitution of $\frac{g_i}{N_i} = e^{\alpha} e^{\beta \epsilon_i} \mp 1$ gives

$$\underline{\ln W_{BE \text{ or } FD} = \sum N_i (\alpha + \beta \epsilon_i) \mp \sum g_i \ln (1 \mp e^{-\alpha} e^{-\beta \epsilon_i})}$$

6.8 cont'd. from Eq. (6.23a), $\ln W_{BE\ or\ FD} = q_{BE\ or\ FD} + \sum N_i(\alpha + \beta\epsilon_i)$

so, by comparison with Eq. (6.29) we obtain

$$\underline{q_{BE\ or\ FD} = \mp \sum g_i \ln(1 \mp e^{-\alpha} e^{-\beta\epsilon_i})}$$

6.9 $$q_B = \ln W_B - \sum(\alpha N_i + \beta\epsilon_i N_i)$$

$$= \sum \underbrace{(N_i \ln g_i - N_i \ln N_i + N_i)}_{= N_i \ln \frac{g_i}{N_i} + N_i \,=\, N_i(\alpha + \beta\epsilon_i) + N_i} - \sum(\alpha N_i + \beta\epsilon_i N_i) = \sum N_i = N$$

or $$\underline{q_B = N = \sum e^{-\alpha} g_i e^{-\beta_i \epsilon_i} = e^{-\alpha} Z}$$

but for $e^{-\alpha} e^{-\beta\epsilon_i} \ll 1$ we can expand $\ln(1 \mp e^{-\alpha} e^{-\beta\epsilon_i})$ and obtain

$$\underline{q_{BE\ or\ FD} \rightarrow \sum g_i e^{-\alpha} e^{-\beta\epsilon_i} = e^{\alpha} Z}$$

6.10 $$\frac{pV}{NkT} = -\frac{1}{\left.\frac{\partial q}{\partial \alpha}\right|_{\beta,V}} q = \frac{\sum(\pm 1)^n e^{-\alpha n}/n^{5/2}}{\sum(\pm 1)^n e^{-\alpha n}/n^{3/2}} = \frac{\sum(\pm 1)^{n-1} e^{-\alpha(n-1)}/n^{5/2}}{\sum(\pm 1)^{n-1} e^{-\alpha(n-1)}/n^{3/2}}$$

$$= \left[\sum(\pm 1)^{n-1} e^{-\alpha(n-1)}/n^{5/2}\right]\left[1 + \left(\pm \frac{e^{-\alpha}}{2^{3/2}} + \frac{e^{-2\alpha}}{3^{3/2}} \pm \frac{e^{-3\alpha}}{4^{3/2}} + \cdots\right)\right]^{-1}$$

$$= \left[1 \pm \frac{e^{-\alpha}}{2^{5/2}} + \frac{e^{-2\alpha}}{3^{5/2}} \pm \cdots\right]\left[1 - (\quad) + (\quad)^2 - (\quad)^3 + \cdots\right]$$

$$\frac{pV}{NkT} = 1 \pm \frac{e^{-\alpha}}{2^{5/2}} \mp \frac{e^{-\alpha}}{2^{3/2}} + \frac{e^{-2\alpha}}{3^{5/2}} \mp \frac{e^{-2\alpha}}{2^{8/2}} + \frac{e^{-2\alpha}}{2^{6/2}} - \frac{e^{-2\alpha}}{3^{3/2}}$$

$$\underline{= 1 \mp \frac{e^{-\alpha}}{2^{5/2}} - \left[\frac{e^{-2\alpha}}{3^{5/2}} - \frac{e^{-2\alpha}}{8}\left[1 \pm \frac{1}{2}\right]\right] + \cdots}$$

& $$U = -\left.\frac{\partial q}{\partial \beta}\right|_{\alpha,V} = +\frac{3}{2}\left(\frac{2\pi mkT}{h^2}\right)^{3/2} kTV \sum \frac{(\pm 1)^n e^{-\alpha n}}{n^{5/2}} = \frac{3}{2} kT q$$

or $$\underline{U = \frac{3}{2} kT\left(N \times \frac{pV}{kT}\right) = \frac{3}{2} NkT\left[1 \mp \frac{e^{-\alpha}}{2^{5/2}} - \left(\frac{e^{-2\alpha}}{3^{5/2}} - \frac{e^{-2\alpha}}{8}\left[1 \pm \frac{1}{2}\right]\right) \cdots\right]}$$

6.11 $$N_i = \frac{g_i}{e^{-(\alpha-\beta\epsilon_i)}-1} \quad \text{or} \quad dN \simeq \frac{\frac{dg}{d\epsilon}\,d\epsilon}{e^{(\mu-\epsilon)/kT}-1}$$

but, with reference to Example 5.2, $g_n = \frac{\pi}{2} n$ so $\frac{dg}{dn} = \frac{\pi}{2} n$. But $n = \sqrt{\frac{8mA}{h^2}}\sqrt{\epsilon}$. Thus, using $\frac{dg}{d\epsilon} = \frac{dg}{dn}\frac{dn}{d\epsilon}$

$$dN = \frac{2\pi m A/h^2}{e^{(\mu-\epsilon)/kT}-1}\,d\epsilon$$

Now let us integrate from ϵ_0 up to ∞ by adding N_{ϵ_0} to the integral from ϵ_0^+ up to ∞. i.e.

$$N = N_{\epsilon_0} + \int_{\epsilon_0^+}^{\infty} \frac{2\pi m A/h^2}{e^{(\mu-\epsilon)/kT}-1}\,d\epsilon$$, or if w call $c \equiv 2\pi m A kT/h^2$

$\eta \equiv (\epsilon-\epsilon_0^+)/kT$

$\xi \equiv \underbrace{e^{(\epsilon_0^+ + \mu)/kT}}_{>1}$

Then
$$N = N_{\epsilon_0} + c\int_0^{\infty} \frac{d\eta}{\frac{1}{\xi}e^{\eta}-1} = N_{\epsilon_0} + c\underbrace{\sum_{m=1}^{\infty}\frac{\xi^m}{m}}_{\text{divergent for } \xi \gg 1}$$

Therefore the particles cannot all cluster at ϵ_0 in this case & there will be no Einstein condensation

6.12 This differs from part 2 of Problem 6.1 only in that we do not use the constraint $\sum N_i = N$. The fifth line in that solution accordingly changes to:

$$\sum\left[(\beta\epsilon_i) + \ln\left(\frac{g_i}{N_i}+1\right)\right]dN_i = 0$$

So.
$$\underline{N_i = \frac{g_i}{e^{\beta\epsilon_i}-1}}$$

Equation (6.17a) becomes $d\ln W = \beta\,\delta Q$

so $dS = d(k\ln W) = \frac{\delta Q}{T} = \beta k\,\delta Q$

Accordingly $\underline{\beta \text{ must} = \frac{1}{kT}}$

6.13 $$q_{BE} = q_{photon} = -\frac{8\pi\sqrt{2}V}{h^3}\cdot\frac{2}{2\sqrt{2}}\left(\frac{h}{c_\ell}\right)^3\int_0^\infty \nu^2 \ln(1-e^{-\beta\epsilon})\,d\nu$$

using $\epsilon = h\nu$ so $\beta\epsilon = h\nu/kT$, and calling $x \equiv h\nu/kT$,

$$q_{photon} = -\left(\frac{2}{c_\ell}\right)^3 \pi V\left(\frac{kT}{h}\right)^3\int_0^\infty x^2\ln(1-e^{-x})\,dx$$

Integrate by parts: $u = \ln(1-e^{-x})$ $\quad dv = x^2dx$

$du = \frac{e^{-x}}{1-e^{-x}}dx \quad v = \frac{x^3}{3}$

so $$\int_0^\infty x^2\ln(1-e^{-x})dx = \frac{x^3}{3}\ln(1-e^{-x})\Big]_0^\infty - \frac{1}{3}\int_0^\infty \frac{x^3e^{-x}}{-(e^x-1)}dx = 0+\frac{\pi^4}{45}$$

finally, $$\underline{q_{photon} = \frac{8\pi^5}{45}V\left(\frac{kT}{c_\ell h}\right)^3}$$

6.14 $$p = \frac{1}{\beta}\frac{\partial}{\partial V}\left[\frac{8\pi^5}{45}\left(\frac{kT}{hc_\ell}\right)^3 V\right] = \frac{1}{\beta}\frac{q}{V}$$ with the help of Eq. (6.33c)

however $U = -\frac{\partial q}{\partial \beta} = +\frac{3}{\beta}q$ so $\underline{pV = \frac{U}{3}}$

Now $$S = k\ln W = kq + k\alpha\underbrace{N}_{\frac{\partial q}{\partial\alpha}=0} + k\beta\underbrace{U}_{\frac{3}{\beta}q} = \underline{4kq = 4\frac{pV}{T}}$$

Finally $$c_v = \frac{\partial U}{\partial T}\Big|_V = 3kT\cdot\frac{4q}{kT} = \underline{\frac{32\pi^5}{15}\left(\frac{kT}{hc_\ell}\right)^3 kV}$$

From Example 1.2, we have $c_v = (16\sigma/c_\ell)T^3V$; but $\sigma = 2\pi^5k^4/15c_\ell^2h^3$ (Eq. (4.39)) so the result is the same.

6.15 For an electron $\Theta_t = \Theta_{t_{H_2}}\frac{m_{H_2}}{m_e} = \mathcal{O}(10^{-11}\,°K)$; hence there was no need to revisit the question. For a photon there is only one quantum level (by the modern quantum theory -- not by Planck's) so the question never arose.

6.16 With reference to Eq. (6.34) we see $q \sim V$ so $p = \frac{1}{\beta}\frac{\partial q}{\partial V}$ or $\frac{1}{\beta}\frac{q}{V}$; and since $q \sim \beta^{-3/2}$, $U = -\frac{\partial q}{\partial \beta} = \frac{3}{2}\frac{q}{\beta}$

Thus $\underline{pV = \frac{2}{3} U}$

Then from Eq. (6.35a) $\quad \frac{pV}{kTN} = 1 \mp \frac{e^{-\alpha}}{2^{5/2}} + \cdots$

but $\quad \alpha = -\frac{\mu_0}{kT} = -\frac{5.51\,eV \times 1.6 \times 10^{-12}\,erg/eV}{1.38 \times 10^{-16} \times 300\,erg} = -213$

so $\frac{pV}{kTN}$ expression won't converge

$\therefore \quad p = kT\frac{N}{V}$

and from Eq. (6.25), $\frac{N}{V} = -\frac{1}{V}\frac{\partial q}{\partial \alpha} = (2\pi mkT/h^2)^{3/2} \times \sum_1^\infty \frac{-ne^{-\alpha n}}{n^{5/2}}$

$$p = (kT)^{5/2}\left(\frac{2\pi m}{h^2}\right)^{3/2}\left[e^{-\alpha} + \sim 0\right]$$

$$= (4.14)^{5/2}\,10^{-35}\left[\frac{6.28(9.109 \times 10^{-28})}{[6.626 \times 10^{-27}]^2}\right]^{3/2} e^{-213}$$

$$= \underbrace{34.8 \times 1.49 \times 10^{-35+39}\,e^{-213}}_{\text{This is an inconceivably small number -- not even worth calculating}}\quad \underbrace{\underbrace{erg^{5/2}\left(\frac{gm}{erg^2 sec^2}\right)^{3/2}}_{dyne^{5/2}\,cm^{5/2}\left[\frac{dyne^{3/2}sec^3/cm^{3/2}}{dyne^3 cm^3 sec^3}\right]}}_{dyne/cm^2}$$

Notice that if T were 3000°K instead of 300°K then

$$p = 34.8 \times 1.49 \times 10^{-35+39} \times 10^{5/2} \times e^{-21.3}$$

$$= \underline{0.13\ dyne/cm^2}$$

so p is very Temperature-sensitive in this range

6.17 $\quad \bar{\epsilon} = \frac{m_e}{2} v_{rms}^2 = \frac{3}{5}\mu_0 \qquad \therefore \qquad \underline{v_{rms} = \sqrt{\frac{6}{5}\frac{\mu_0}{m_e}}}$

To evaluate $\bar{v}$ we need $F(v)$ since $\quad \bar{v} = \frac{1}{\sqrt{2\mu_0/m_e}} \int_0^{\sqrt{2\mu_0/m_e}} v\, F(v)\, dv$

Using Eq. (6.42) for $f(\epsilon)$,

$$F(v) = \frac{1}{N} f(\epsilon) = \frac{4\pi V}{N}\left(\frac{2m_e}{h^2}\right)^{3/2} \frac{\sqrt{\frac{m_e}{2}}\, v}{\underbrace{e^{(\epsilon-\mu)/kT}}_{e^{-\infty} \to 0} - 1}$$

so

$$\bar{v} = 4\pi \frac{V}{N}\left(\frac{2m_e}{h^2}\right)^{3/2} \sqrt{\frac{m_e}{2\mu_0}} \cdot \sqrt{\frac{m_e}{2}} \int_0^{\sqrt{2\mu_0/m_e}} v^2\, dv = \frac{16\pi V}{3N}\left(\frac{2m_e\mu_0}{h^2}\right)^{3/2} \sqrt{\frac{\mu_0}{m_e}}$$

but from Example 6.3, $\left(\frac{2m_e\mu_0}{h^2}\right)^{3/2} = \frac{3}{\pi}\frac{N}{V}\frac{1}{8^{3/2}}$ so

$$\underline{\bar{v} = \frac{2}{\sqrt{8}}\sqrt{\frac{\mu_0}{m_e}} = \sqrt{\frac{1}{2}\frac{\mu_0}{m_e}} = \sqrt{\frac{5}{12}}\, v_{rms}}$$

6.18 The electron flux is:

$$J_e = \frac{n\bar{v}}{4} = \frac{N}{V}\sqrt{\frac{1}{32}\frac{\mu_0}{m_e}}$$

where $N/V = 5.8\times10^{22}$ electrons/cm^3 (Table 6.1)

$$J_e = 5.8\times10^{22}\sqrt{\frac{1}{32}\,\frac{5.51\times1.6\times10^{-12}}{9.11\times10^{-28}}}\ \frac{\text{electron}}{\text{cm}^3}\sqrt{\frac{\text{erg}}{\text{gm}}}$$

$$\underline{= \overset{1.01}{\cancel{1.02}}\times10^{\overset{30}{\cancel{29}}}\ \frac{\text{electrons}}{\text{cm}^2\ \text{sec}}}$$

but the charge on an electron is -1.602×10^{-19} Coulomb

so

$$\underline{I = -1.61\times10^{10}\ \frac{\text{Coulomb}}{\text{cm}^2\ \text{sec}} = 1.61\overset{6}{\wedge}\times10^{\overset{11}{\cancel{10}}}\ \frac{\text{Amp}}{\text{cm}^2}}$$

which would be an enormous current

6.19

$$F(\epsilon) = \frac{1}{N} f(\epsilon) = 4\pi\left(\frac{2m}{h^2}\right)^{3/2} \frac{V}{N} \frac{\sqrt{\epsilon}}{e^{(\epsilon-\mu)/kT}+1}$$

where V/N is given by Richtmayer et al. (footnote 4-1) pg 101 as 6.6×10^{22} electrons/cm^3 and

$$\frac{\mu}{\mu_0} \simeq 1 - \frac{\pi^2}{12}\left(\frac{k}{\mu_0}\right)^2 T^2 \quad \text{\&} \quad \mu_0 = \frac{\frac{\pi^2}{2} k R^\circ}{A} = \frac{\pi^2\, 1.38\times 8.31\times10^{-16+7}}{2\times16.25\times10^{-4}/.239\times10^{-7}}$$

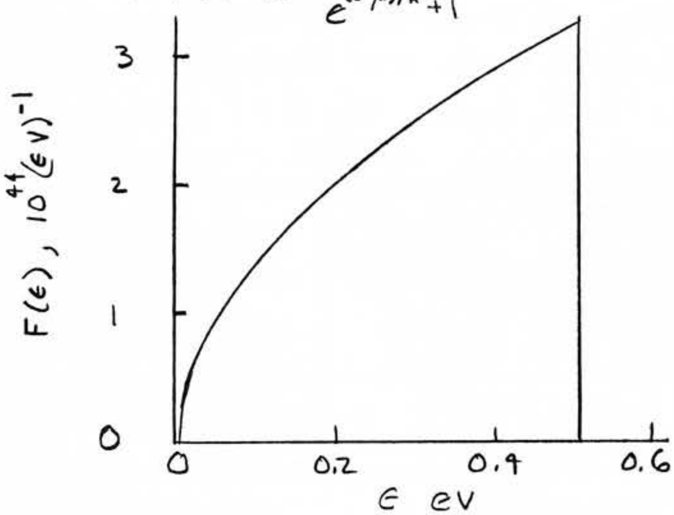
$$= .836\times10^{-12}\,erg = .522\,eV$$

$$\mu = .522\left[1 - 2.24\times10^{-8}T^2\right]$$

so

$$F(\epsilon) = 3.39\times10^{39}\times(6.6\times10^{22})\times\left[1.6\times10^{-12}\right]^{-3/2}\frac{\sqrt{\epsilon}}{e^{(\epsilon-\mu)/kT}+1}$$

$$= 4.55\times10^{44}\frac{\sqrt{\epsilon}}{e^{(\epsilon-\mu)/kT}+1}$$

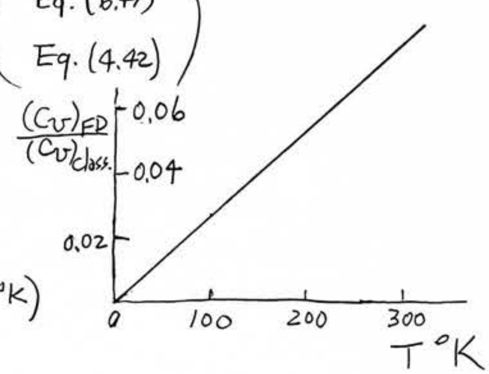


$$\frac{(C_v)_{FD}}{(C_v)_{classical}} = \frac{\frac{\pi^2}{2}\left(\frac{kT}{\mu_0}\right)R^\circ}{3R^\circ} \quad \left(\begin{array}{c}\text{Eq. (6.47)}\\ \text{Eq. (4.42)}\end{array}\right)$$

$$= \frac{\pi^2}{6}\left(\frac{k}{\mu_0}\right)T$$

$$= \frac{3.14^2}{6}\,\frac{1.38\times10^{-16}}{0.836\times10^{-12}}\,T$$

$$= 2.7\times10^{-4}\,T \quad (T\ {}^\circ K)$$



CHAPTER 7

7.1 Stirling's approximation is $\ln N! \simeq \ln\left(\frac{N}{e}\right)^N$ so

$$\ln W_{indist} = \ln\left(\frac{Z^N}{N!} e^{U/kT}\right) \simeq \underline{\ln\left(\left[\frac{Ze}{N}\right]^N e^{U/kT}\right)} \qquad (7.3a)$$

so

$$S_{indist} = k \ln W = kN \ln Z + \frac{U}{T} - k \ln N!$$
$$= \underline{S_{dist} - k \ln N!} \qquad (7.5)$$

7.2 The properties T and V are independent and not listed.

The properties p, U, $H = U + pV$, c_p and c_v all depend upon the derivatives of $\ln Z$ with respect to variables other than N and will be same in either case.

The quantities S, $F = U - TS$, $G = H - TS$, and $\mu = (\partial F/\partial N)_{T,V}$ can all be got from the Sackur-Tetrode equation for S_{indist} and from Eq. (7.5) above

	indistinguishable	distinguishable
S	$\underline{kN\left\{\ln\left[\left(\frac{2m\pi kT}{h^2}\right)^{3/2}\frac{kT}{p}\right]+\frac{5}{2}\right\}}$	$kN\left\{\left[\ln\left(\frac{2m\pi kT}{h^2}\right)^{3/2}\frac{kT}{p}\right]+\frac{3}{2}\right\}$
F	$-kNT\left\{\ln\left[\left(\frac{2\pi mkT}{h^2}\right)^{3/2}\frac{kT}{p}\right]+1\right\}$	$-kNT\ \ln\left[\left(\frac{2\pi mkT}{h^2}\right)^{3/2}\frac{kNT}{p}\right]$
G	$-kNT\ln\left[\left(\frac{2\pi mkT}{h^2}\right)^{3/2}\frac{kT}{p}\right]$	$-kNT\left\{\ln\left[\left(\frac{2\pi mkT}{h^2}\right)^{3/2}\frac{kNT}{p}\right]-1\right\}$
μ	$-kT\ \ln\left[\left(\frac{2\pi mkT}{h^2}\right)^{3/2}\frac{kT}{p}\right]$	$-kT\left\{\ln\left[\left(\frac{2\pi mkT}{h^2}\right)^{3/2}\frac{kNT}{p}\right]+1\right\}$

An attempt to treat S, F, G or μ as distinguishable when it is not will lead to error. Note in particular that μ can only be truly <u>intensive</u> (<u>i.e.</u> independent of N) when particles are indistinguishable.

7.3 This is an open-ended exercise.

7.4 $$\frac{S}{R^o} = \ln\left[\left(\frac{U}{U_o}\right)^{3/2}\left(\frac{V}{V_o}\right)\left(\frac{N_o}{N}\right)^{5/2}\right] = \ln\left[\left(\frac{2\pi m}{h^2}\right)^{3/2}\frac{V}{N}(kT)^{3/2}e^{5/2}\right]$$

in consistent units. But $U = \frac{3}{2}NkT$ so

$$\ln\left[\frac{N_o^{5/2}}{U_o^{3/2}V_o}\cdot\frac{U^{3/2}V}{N^{5/2}}\right] = \ln\left[\left(\frac{2\pi m}{h^2}\right)^{3/2}e^{5/2}\left(\frac{2}{3}\right)^{3/2}\frac{U^{3/2}V}{N^{5/2}}\right]$$

so

$$\underline{\frac{N_o^{5/2}}{U_o^{3/2}V_o} = \left(\frac{4\pi m e}{3h^2}\right)^{3/2} e}$$

7.5 $$Z_e = \sum_{i=0}^{\infty} g_{e_i}\exp(-\epsilon_i/kT) = g_{e_o}e^0 + \sum_{i=1}^{\infty} g_i e^{\sim\infty} = \underline{g_{e_o}}$$

$$U = kT^2 N_A \underbrace{\frac{\partial \ln Z}{\partial T}}_{=0} = \underline{0} \quad ; \quad H = U + \underbrace{pV}_{\text{meaningless for rotation}} = \underline{0}$$

$$c_p = \frac{\partial H}{\partial T} = c_v = \frac{\partial U}{\partial T} = \underline{0}$$

$$S = kN_A \ln Z + \frac{U}{T} = \underline{R^o \ln g_{e_o}} \; ; \quad F = G = -TS = \underline{-R^oT\ln g_{e_o}}$$

$$\underline{Z_D = \sum g_{D_i} e^{-(-D/kT)} = \underline{e^{D/kT}}}$$ since only one level & $g_D = 1$

$$U_D = kT^2 N_A \frac{\partial \ln Z}{\partial T} = \underline{-N_A D}\,, \quad H = U = \underline{-N_A D}$$

$$S = kN_A \ln Z + \frac{U}{T} = \frac{N_A D}{T} - \frac{N_A D}{T} = \underline{0}$$ (no disorder involved here)

$$F = U - TS = \underline{-N_A D}\,, \quad G = H - TS = \underline{-N_A D}$$

$$c_p = \frac{\partial H}{\partial T} = c_v = \frac{\partial U}{\partial T} = \underline{0}$$

7.6 $Z_t \sim T^{3/2}$, $Z_r \sim T$, $Z_v \sim T$. Therefore

$$\frac{c_v}{R^o} = \frac{\partial}{\partial T}\left(T^2\left[\frac{\partial \ln T^{3/2}}{\partial T} + \frac{\partial \ln T}{\partial T} + \frac{\partial \ln T}{\partial T}\right]\right) = \frac{\partial}{\partial T}\left(T^2\left[\frac{3}{2T} + \frac{2}{T}\right]\right) = \underline{\frac{7}{2}}$$

And this is exactly the result we obtained in Sec. 3.7.

7.7 $$\Theta_v = \frac{h\nu}{k} = \frac{6.626\times10^{-27}\,\text{erg-sec}\ 10^{13}\,\text{rad/sec}}{(1.38\times10^{-16}\,\text{erg}/^o\text{K})\,2\pi\,\frac{\text{rad}}{\text{cps}}} = 76.4^oK < 300^oK$$

$\therefore$ the energy spacings should be getting fairly close

$$\frac{N_i}{N} = \frac{\exp(-[\frac{1}{2}+i]h\nu/kT)}{[2\sinh[\Theta_v/2T]]^{-1}} = 0.255\ \exp\left[-(\tfrac{1}{2}+i)(.2545)\right]$$

$i=0$, $\frac{N_0}{N} = 0.224$

$i=1$, $\frac{N_1}{N} = 0.174$

$i=2$, $\frac{N_2}{N} = 0.135$

$i=3$, $\frac{N_3}{N} = 0.104$

$i=4$, $\frac{N_4}{N} = 0.082$

Since the energy spacings aren't wide, we would not expect fairly rapid convergence.

$$\sum_{i=0}^{4}\frac{N_i}{N} = \underline{0.719} < 1,$$ which means that $i=0$ to 4 would include most of the excited energy states.

7.8 Θ_t should be computed from the expression atop pg 178 and based upon an assumed V.

$$\Theta_r = \frac{\hbar^2}{2Ik} \quad ; \quad I = \left(2\,\frac{m_{N_2}}{2}\right)\left(\frac{\text{spacing}}{2}\right)^2 = \frac{28}{N_A}\left(\frac{1.098\text{Å}}{2}\,10^{-8}\frac{\text{cm}}{\text{Å}}\right)^2 = 1.4\times10^{-39}$$

$$\Theta_r = \frac{(1.054)^2\times10^{-54}}{2.8\times10^{-39}(1.38\times10^{-16})} = \underline{2.87^oK}$$ (Table 7.2 gives 2.89°K)

$$\Theta_v = \frac{h\nu}{k} = \frac{h}{k}k_e c_\ell = \frac{6.626\times10^{-27}}{1.38\times10^{-16}}2358(3\times10^{10}) = \underline{3395^oK}$$

(Table 7.2 gives 3390°K)

7.9 $\psi_r = \frac{1}{\sqrt{2\pi}}\left[\frac{(2\ell+1)(\ell-m)}{2(m+\ell)}\right]^{1/2} P_\ell^m \underbrace{(\cos[\pi-\theta])}_{=\cos\theta} \underbrace{e^{im(\phi+\pi)}}_{e^{im\phi}\ \underbrace{e^{im\pi}}_{\underbrace{\cos m\pi}_{(-1)^m} + \underbrace{i\sin m\pi}_{=0}}}$

Thus ψ changes sign, and is antisymmetric, when the ends of the molecule are interchanged, only for m-odd. But $m \le \ell$ and the largest value of m, namely ℓ, will be the one that specifies simple rotation. Thus

$$\underline{\psi_r(\pi-\theta, \phi+\pi) = (-1)^\ell\ \psi_r(\theta,\phi)}$$

7.10 $Z = Z_n Z_n Z_r$ but (cf. Eq. (7.23)) $Z_n = g_n$ and we must divide by the σ indistinguishable orientations.

Thus $\underline{Z = (g_n^2/\sigma) Z_r}$

7.11
7.12 This is essentially a slide-rule exercise paralleling Example 7.2. The experimental values against which it should check, are

$S = 70.776$ cal/gmole°K and $H = 35{,}276$ cal/gmole

so $G = H - TS = \underline{-247{,}224 \text{ cal/gmole}}$. In Problem
7.13 7.13 there will be no significant contribution of vibration.

7.14 $I_{O\text{-}O} = m_O r_O^2 + m_O r_O^2 = \underline{2 m_O r_O^2}$

$I_{H\text{-}N}$; first locate the c.g.: $\Sigma m_i r_i = 0$

or $m_N r_{NO} - m_C r_{CO} - m_H(r_{HC} + r_{CO}) = 0$

where O is the c.g.. Now $r_{NO} + r_{CO} = r_{CN}$ so we can show that

$$r_{NO} = \frac{m_C r_{CN} + m_H(r_{CN} + r_{HC})}{m_H + m_C + m_N}$$

then

$I_{H\text{-}H}$ = (I about axis passing thru N, $\perp$ to HCN) − (I about axis thru O, $\perp$ to HCN)

$$I_{H\text{-}N} = m_C r_{CN}^2 + m_H (r_{CN} + r_{CH})^2 - \frac{[m_C r_{CN} + m_H (r_{CN} + r_{CH})]^2}{m_N + m_C + m_H}$$

I_{H_2O} ; center of mass, $m_O r_{O\text{-}O} - 2m_H (r_H \cos\theta - r_{O\text{-}O}) = 0$

$$r_{O\text{-}O} = \frac{2m_H r_H \cos\theta}{m_O + 2m_H}$$

$$I_x = 2m_H r_H^2 \cos^2\theta - (m_O + 2m_H) r_{O\text{-}O}^2$$

$$= \underline{2m_H r_H^2 \cos^2\theta \left[1 - \frac{2m_H}{m_O + 2m_H}\right]}$$

$$\underline{I_z = 2m_H r_H^2 \sin^2\theta}$$

$$\underline{I_y = I_x + I_y}$$

For methane, $r_{CH} = 1.091\,\text{Å}$; $(2\theta)_{HCH} = 109.5°$ and the c.g. is located at the carbon molecule.

$$r_{H-H} = 2r_{C-H} \sin\Theta_{HCH} = 1.79\,\text{Å}$$

$$\underbrace{r_{OH}}_{\text{projection } \perp \text{ to AXIS}} = r_{H\text{-}H} \sin\Theta_{CHH} = 2.18 \sin\left(\frac{180-109.5}{2}\right) = 0.92\,\text{Å}$$

$$I_{AA} = I_{BB} = I_{CC} = I_{DD} = 3m_H r_{OH}^2 = \underline{.423 \times 10^{-39}\ \text{gm cm}^2}$$

7.15 $$d\ln W + \sum_\alpha \left\{ d\sum_i \alpha N_{\alpha_i} + d\sum_i \beta\epsilon_{\alpha_i} N_{\alpha_i} \right\} = 0$$

$$\sum_\alpha \left\{ \sum_i \left[\ln(g_{\alpha_i}/N_{\alpha_i}) + \alpha + \beta\epsilon_{\alpha_i} \right] dN_{\alpha_i} \right\} = 0$$

so: $N_{\alpha_i} = g_{\alpha_i} e^{-\alpha} e^{-\beta\epsilon_{\alpha i}}$

& $\underline{N_{\alpha_i} = \frac{N_\alpha}{Z_\alpha} g_{\alpha_i} e^{-\beta\epsilon_{\alpha_i}}}$; $\underline{Z_\alpha = \sum_i g_{\alpha_i} e^{-\beta\epsilon_{\alpha_i}}}$

Nothing in the context of equations (6.17) and (6.18) changes, so that proof of $\beta = 1/kT$ still applies here.

7.16 $\mu = -kN_AT \ln \frac{Z_\alpha}{N_\alpha} = R^\circ T\left[\ln \frac{1}{Z_\alpha} + \ln N_\alpha \underbrace{- \ln p_\alpha}_{\ln N_\alpha kT/V} + \ln p_\alpha\right]$

$$= R^\circ T \left\{ \underbrace{\ln\left[\frac{V}{kT Z_\alpha(T,V)}\right]}_{\equiv \phi_\alpha(T)} + \ln p_\alpha \right\}$$

but $\phi_{\text{classical}} = (\mu_\alpha / R^\circ T) - \ln p_\alpha \equiv \phi_\alpha(T)$

7.17 While Nimrod lives: $\Delta S_{mix} = -(3+2)R^\circ\left[\frac{2}{5}\ln\frac{2}{5} + \frac{3}{5}\ln\frac{3}{5}\right] = \underline{+6.66 \frac{cal}{{}^\circ K}}$

If Nimrod died before mixing, there would be no operational means for asserting that mixing had occured, so $\underline{\Delta S_{mix} = 0}$. However we must admit that quantum mechanics denies that Nimrod could have existed in the first place. For him to have made the distinction when no other test conceivably could, would require that he function below the level of the Uncertainty Principle; And that would not be possible.

7.18 a.) $p_f = (n_1+n_2)R^\circ T/(V_1+V_2) = \frac{(n_1+n_2)R^\circ T}{\frac{n_1 R^\circ T}{p_1} + \frac{n_2 R^\circ T}{p_2}} = \underline{(n_1+n_2)\frac{p_1 p_2}{n_1 p_2 + n_2 p_1}}$

b.) $\Delta S_{mix} = -n_1 R^\circ \ln \frac{V_f}{V_1} - n_2 R^\circ \ln \frac{V_f}{V_2}$

$$= -n_1 R^\circ \ln \frac{p_f / n_f R^\circ T}{p_1 / n_1 R^\circ T} - n_2 R^\circ \ln \frac{p_f / n_f R^\circ T}{p_2 / n_2 R^\circ T} = \underline{R^\circ\left[n_1 \ln \frac{p_f n_1}{p_1 n_f} + n_2 \ln \frac{p_f n_2}{p_2 n_f}\right]}$$

where $n_f = n_1 + n_2$.

c.) ΔS_{mix} = same as in b.) unless $p_1 = p_2$. Then $\Delta S_{mix} = 0$.

d.) $\Delta S_1 = -n_1 R^\circ \ln \frac{V_f}{V_1} = n_1 R^\circ \ln \frac{p_f n_1}{p_1 n_f}$

$\Delta S_2 = -n_2 R^\circ \ln \frac{V_f}{V_2} = n_2 R^\circ \ln \frac{p_f n_2}{p_2 n_f}$

& the sum is exactly the result of b.) once more.

7.19 $$d\ln W - \alpha_X\, d\Big(\sum_i N_{X_i} + \sum_i N_{XY_i}\Big) - \alpha_Y\, d\Big(\sum_i N_{Y_i} + \sum_i N_{XY_i}\Big)$$
$$-\beta\, d\Big(\sum N_{X_i}\epsilon_{X_i} + \sum_i N_{Y_i}\epsilon_{Y_i} + \sum_i N_{XY_i}(\epsilon_{XY_i} - D_0)\Big) = 0$$

so

$$\sum_i \Big\{\Big(\ln\frac{g_{X_i}}{N_{X_i}} - \alpha_X - \beta\,\epsilon_{X_i}\Big)dN_{X_i} + \Big(\ln\frac{g_{Y_i}}{N_{Y_i}} - \alpha_Y - \beta\,\epsilon_{Y_i}\Big)dN_{Y_i}$$
$$+ \Big(\ln\frac{g_{XY_i}}{N_{XY_i}} - (\alpha_X + \alpha_Y) - \beta[\epsilon_{XY_i} - D_0]\Big)dN_{XY_i}\Big\} = 0$$

The coefficients must vanish identically so

$$\underline{N_{X_i} = g_{X_i} e^{-\alpha_X} e^{-\beta\epsilon_{X_i}}} \;; \qquad \underline{N_{Y_i} = g_{Y_i} e^{-\alpha_Y} e^{-\beta\epsilon_{Y_i}}}$$

and $$\underline{N_{XY_i} = g_{XY_i} e^{-\alpha_X - \alpha_Y} e^{-\beta(\epsilon_{XY_i} - D_0)}}$$

and where $\beta = 1/kT$ since $k\,d\ln W\big|_{N=\text{const}} = dS = k\beta \underbrace{\delta Q}_{TdS}$

7.20 $$p = -\frac{\partial F}{\partial V} = +kT\sum_\alpha \frac{\partial}{\partial V}\ln\Big(\frac{Z_\alpha e}{N_\alpha}\Big)^{N_\alpha} = kT\sum_\alpha \frac{N_\alpha}{Z_\alpha}\underbrace{\frac{\partial Z_\alpha}{\partial V}}_{Z_\alpha/V} = \underline{\frac{kT}{V}(N_X + N_Y + N_{XY})}$$

$$\mu_X = N_A\frac{\partial F}{\partial N_X} = -N_A kT\frac{\partial}{\partial N_X}\ln\Big[\frac{Z_X e}{N_X}\Big]^{N_X} = \underline{-N_A kT\ln\frac{Z_X}{N_X}}$$

$$\mu_Y = N_A\frac{\partial F}{\partial N_Y} = -N_A kT\frac{\partial}{\partial N_Y}\ln\Big[\frac{Z_Y e}{N_Y}\Big]^{N_Y} = \underline{-N_A kT\ln\frac{Z_Y}{N_Y}}$$

$$\mu_{XY} = N_A\frac{\partial F}{\partial N_{XY}} = -N_A kT\Big[\frac{\partial}{\partial N_{XY}}\Big(\Big[\frac{Z_{XY} e}{N_{XY}}\Big]^{N_{XY}} + \frac{N_{XY}D_0}{kT}\Big)\Big]$$
$$= \underline{-N_A kT\ln\frac{Z_{XY}}{N_{XY}} - N_A D_0}$$

$$\frac{N_{XY}}{N_X N_Y}\cdot\frac{Z_X Z_Y}{Z_{XY}} = \frac{Z_X}{N_X}\cdot\frac{Z_Y}{N_Y}\cdot\frac{N_{XY}}{Z_{XY}} = \underbrace{e^{-\frac{\mu_X}{N_A kT}} e^{-\frac{\mu_Y}{N_A kT}} e^{+\frac{\mu_{XY} + N_A D_0}{N_A kT}}}_{-\mu_x - \mu_y + \mu_{xy} = 0} = e^{\frac{D_0}{kT}}$$

$$\underline{-\mu_x - \mu_y + \mu_{xy} = 0}$$

7.21 The same development that Eqs. (7.77) → (7.80), yields for the general case:

$$\prod_\alpha N_\alpha^{-\nu_\alpha} \cdot \prod_\alpha Z_\alpha^{+\nu_\alpha} = \exp\left[\frac{-D_0}{kT}\right]$$

or

$$\prod_\alpha \left(\frac{Z_\alpha}{N_\alpha}\right)^{\nu_\alpha} = \exp\left[\sum_\alpha\left(\frac{\nu_\alpha \mu_\alpha}{kT}\right) - \frac{D_0}{kT}\right] = \exp\left[\frac{-D_0}{kT}\right]$$

so $\underline{\sum_\alpha \nu_\alpha \mu_\alpha = 0}$

and

$$K(T) \equiv \left[\prod_\alpha \left(Z_\alpha^{\nu_\alpha}\right) \exp\left(\frac{D_0}{kT}\right)\right] = \underline{\prod_\alpha N_\alpha^{\nu_\alpha}}$$

or

$$K(T) = \left[\prod_\alpha \left(\frac{Z_\alpha}{p}\right)^{\nu_\alpha} \exp\left(\frac{D_0}{kT}\right)\right] = \prod_\alpha (pN_\alpha)^{\nu_\alpha}$$

$$\underline{K(T) = \left[\prod_\alpha \left(\frac{Z_\alpha kT}{V}\right)^{\nu_\alpha} \exp\left(\frac{D_0}{kT}\right) = \prod_\alpha p_\alpha^{\nu_\alpha}\right.}$$

7.22 $\ln K(T) = \sum \nu_\alpha \ln p_\alpha$ but $\frac{\mu_\alpha}{R^0 T} + \ln p_\alpha = \phi_\alpha$

$$\therefore \quad \underline{\ln K(T) = \sum \nu_\alpha \phi_\alpha} - \underbrace{\sum \nu_\alpha \mu_\alpha / R^0 T}_{=0 \text{ since } \sum \nu_\alpha \mu_\alpha = 0}$$

7.23 we can write: $-\frac{h_\alpha}{T^2} = -\frac{s_\alpha}{T} - \left[\frac{h_\alpha}{T^2} - \frac{s_\alpha}{T}\right] = -\frac{s_\alpha}{T} - \frac{g_\alpha}{T^2}$

but $\left.\frac{\partial g_\alpha}{\partial T}\right|_p = -s$ so $-\frac{h_\alpha}{T^2} = \frac{1}{T}\frac{\partial g_\alpha}{\partial T} - \frac{g_\alpha}{T^2} = \frac{\partial(g_\alpha/T)}{\partial T}$

Then noting that $g_\alpha/T = R^0 \phi_\alpha + R^0 \ln p_\alpha$ we get:

$$\underline{h_\alpha = -R^0 T^2 \frac{\partial \phi_\alpha}{\partial T}}$$

so $\Delta h = \sum_\alpha \nu_\alpha h_\alpha = -R^0 T^2 \sum \nu_\alpha \frac{\partial \phi_\alpha}{\partial T}$, but $\ln K_p = -\sum \nu_\alpha \phi_\alpha$

so $\underline{\Delta h = R^0 T^2 \frac{\partial \ln K_p}{\partial T}}$

7.24 $\Delta h = R^\circ T^2 \dfrac{d\ln K}{dT} = -R^\circ\left(\dfrac{d\ln K}{d(1/T)}\right)$

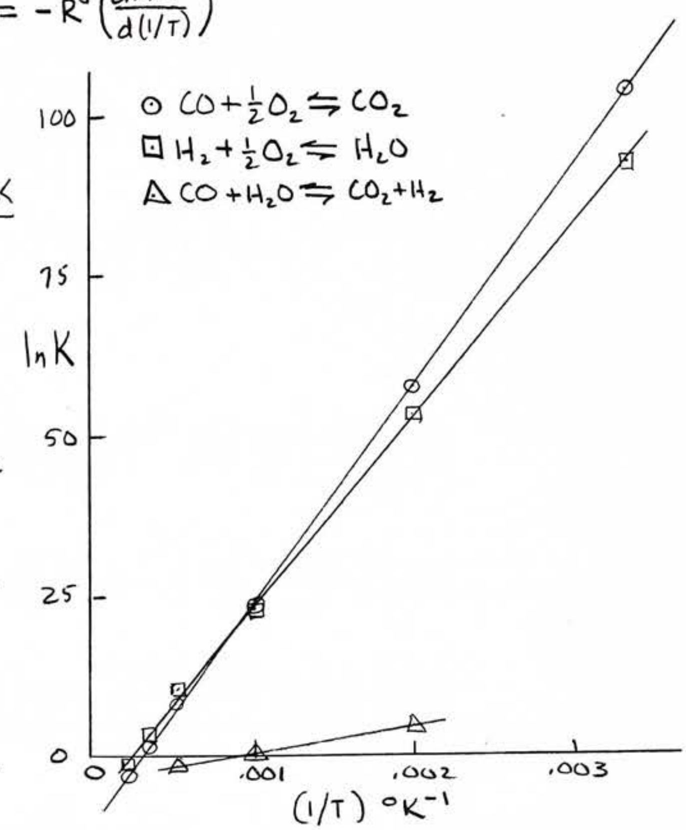
At 1000°F

	$-d\ln K/d(\frac{1}{T})$, °K
⊙	34,100
⊡	30,000
△	4,380

So

	Δh cal/gmole	
	van't Hoff	expt'l.
⊙	-67,700	-67,601
⊡	-59,600	-59,199
△	-8,700	-8,403

The comparison is completely accurate within plotting error.



7.25 Some H_2O goes to H_2 & O_2 while some goes to H_2 & OH.

$$H_2O \rightleftharpoons H_2 + \tfrac{1}{2}O_2 \;,\quad K_{O_2} = \text{anti}\ln(-3.8) = 0.0225$$
$$-a \qquad a \qquad \tfrac{1}{2}a \longleftarrow a \text{ moles of } H_2O \text{ do this}$$

and

$$H_2O \rightleftharpoons \tfrac{1}{2}H_2 + OH \qquad K_{OH} = \text{anti}\ln(-3.745) = 0.0235$$
$$-b \qquad \tfrac{1}{2}b \qquad b \longleftarrow b \text{ moles of } H_2O \text{ do this}$$

and $1-a-b$ moles of H_2O remain. The number of moles of mixture at any moment is then $1+\frac{1}{2}a+\frac{1}{2}b$.

Then

$$K_{O_2} = 0.0225 = \frac{x_{H_2}\sqrt{x_{O_2}}}{x_{H_2O}}\,p^{1+\frac{1}{2}-1} = \frac{\left(\frac{a+b/2}{1+\frac{1}{2}a+\frac{1}{2}b}\right)\left(\frac{a/2}{1+\frac{1}{2}a+\frac{1}{2}b}\right)^{1/2}}{(1-a-b)/(1+\frac{1}{2}a+\frac{1}{2}b)}$$

$$K_{OH} = 0.0235 = \frac{\sqrt{x_{H_2}}\,x_{OH}}{x_{H_2O}}\,p^{1/2+1-1} = \frac{\left(\frac{a+b/2}{1+\frac{1}{2}a+\frac{1}{2}b}\right)^{1/2}\left(\frac{b}{1+\frac{1}{2}a+\frac{1}{2}b}\right)}{(1-a-b)/(1+\frac{1}{2}a+\frac{1}{2}b)}$$

.068 .066 are closer but not there

These two equations in a and b can be solved by trial and error. With a little crafty guessing we obtain: $a = \underline{\cancel{0.053}}$ & $b = \underline{\cancel{0.071}}$ so

.01 $$x_{H_2O} = \frac{1-.053-.071}{1+\cancel{.0265}+\cancel{.0355}} = \underline{\cancel{0.825}} \quad ; \quad x_{O_2} = \frac{\cancel{0.0265}}{\cancel{1.062}} = \underline{\cancel{0.0249}}$$

$$x_{H_2} = \frac{\cancel{0.053+0.071}/2}{\cancel{1.062}} = \underline{\cancel{0.1178}} \quad ; \quad x_{OH} = \frac{\cancel{0.071}}{\cancel{1.062}} = \underline{\cancel{0.0668}}$$

7.26 Substituting the appropriate numbers in Eq. (7.120),

$$\rho_D = \frac{16}{6.02\times10^{23}}\left[\frac{\pi\left(\frac{16}{6.02}\times10^{-23}\right)(1.38\times10^{-16})}{(6.626\times10^{-27})^2}\right]^{3/2} 2.08\sqrt{4000}\left(1-e^{-\frac{2230}{4000}}\right)\frac{9^2}{3} = \underline{171\ \frac{gm}{cm^3}}$$

which disagrees by 9% from Lighthill's value of 156.

7.27 First we need an entropy expression.

$$S = S_{Argon} + S_{Ionized\ Argon} + S_e$$

$$= (1-\epsilon)Nk\left[\ln\left(\frac{2\pi m_A kT}{h^2}\right)^{3/2}\frac{e^{5/2}V}{(1-\epsilon)N} + \ln Z_{A_{int}} + T\frac{\partial \ln Z_{A\,int}}{\partial T}\right]$$

$$+ \epsilon Nk\left[\ln\left(\frac{2\pi m_I kT}{h^2}\right)^{3/2}\frac{e^{5/2}V}{\epsilon N} + \ln Z_{I\,int} + T\frac{\partial Z_{I\,int}}{\partial T}\right]$$

$$+ \epsilon Nk\left[\ln\left[\frac{2\pi m_e kT}{h^2}\right]^{3/2}\frac{e^{5/2}V}{\epsilon N} + \ln \underbrace{Z_e}_{=2} + 0\right]$$

Setting $m_A = m_I$ and $V = \frac{1+\epsilon}{p}NkT$ we get

$$S = Nk\left\{(1+\epsilon)\left[\frac{5}{2} + \frac{5}{2}\ln T - \ln p + \ln\frac{(2\pi)^{3/2}k^{5/2}}{h^3}\right]\right.$$

$$+ (1-\epsilon)\left[\frac{\frac{3}{2}\ln m_A}{1-\epsilon} + \ln Z_{A_{int}} + T\frac{\partial \ln Z_{A\,int}}{T} - \ln\frac{1-\epsilon}{1+\epsilon}\right]$$

$$\left. + \epsilon\left[\frac{3}{2}\ln m_e + \ln Z_{I_{int}} + T\frac{\partial Z_I}{\partial T} + \ln 2 - 2\ln\frac{\epsilon}{1-\epsilon}\right]\right\}$$

Substitution of the Saha equation in this gives,

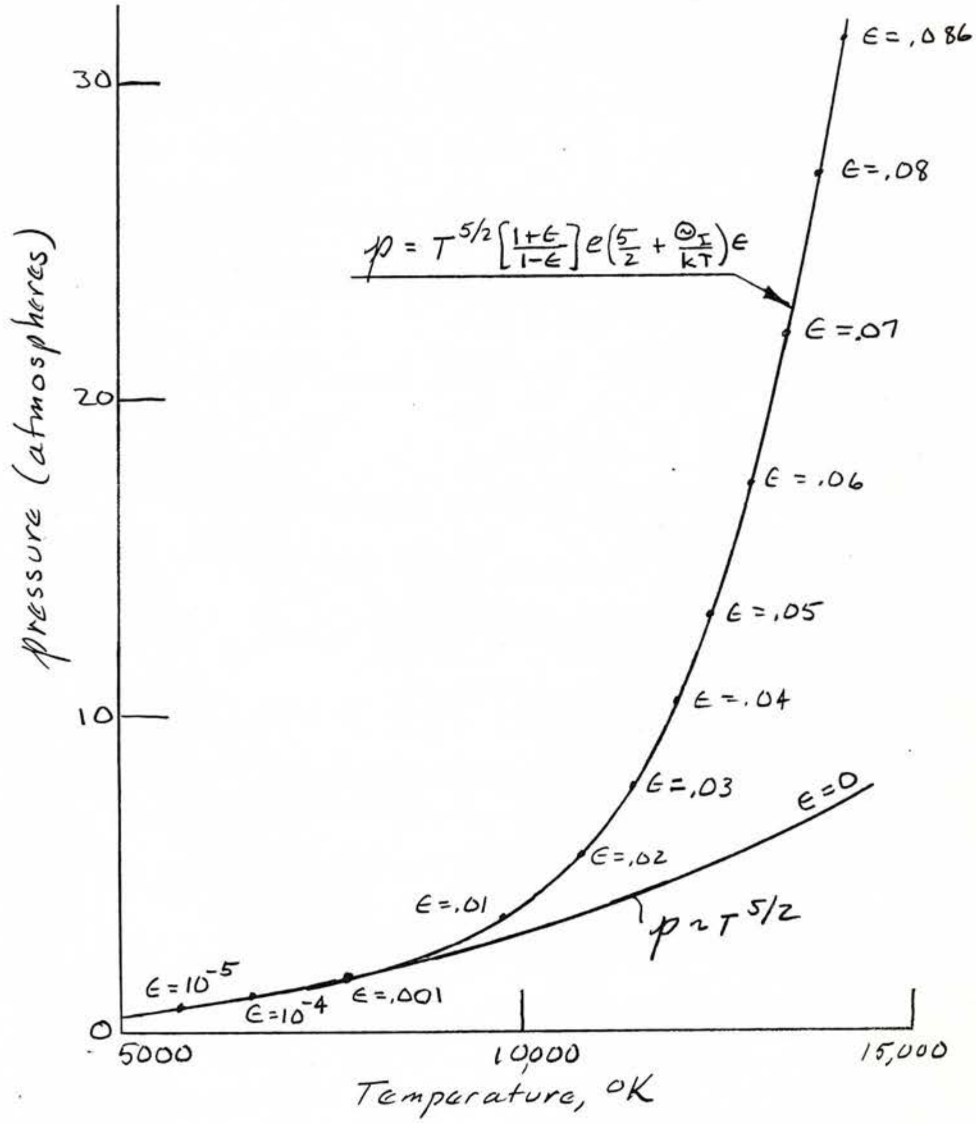
$$S = Nk\left\{\ln\left(\frac{2\pi m_A}{h^2}\right)^{3/2}k^{5/2} + \frac{5(1+\epsilon)}{2} + \ln\frac{1+\epsilon}{1-\epsilon}\frac{T^{5/2}}{p} + \ln Z_{A_{int}} + T\frac{\partial \ln Z_{A\,int}}{\partial T}\right.$$

$$\left. - \epsilon\left(T\frac{\partial}{\partial T}\ln\frac{Z_{A\,int}}{Z_I} - \frac{\Theta_I}{kT}\right)\right\}$$

7.27 Cont'd. But $Z_{A_{int}} = g_{A_0} = $ const., so in a constant S process this expression gives

$$\text{Const.} = \frac{1+\epsilon}{1-\epsilon}\,\frac{T^{5/2}}{p}\,e^{\epsilon\left(\frac{5}{2}+\frac{\Theta_I}{kT}\right)}$$

and as $\epsilon \to 0$, $C = T^{5/2}/p$



Full detail is given by J. Pomerantz, E. H. Winkler, A. E. Siegel, "Thermodynamic Properties and 1-Dim. Flow of a Partially Ionized Monatomic Gas," NAVORD Rept. 4222, 2 Feb. '56.

7.28 See above report. (This Problem is quite complex.)

Chapter 8

8.1 It is our experience that students frequently have trouble manufacturing analogies of this kind. There are never-the-less, no end to the possibilities. 8.11 is one example. Another is:

A certain large university offers many sections of Introductory Thermodynamics. All classes are the same size and, since the computer places the students randomly, the average intelligence is the same in each section. The students can exchange information outside of class but they cannot exchange themselves nor their native abilities. Setting the analogy thus: N_α = no. students in a section, T_α = avg. intelligence in a section, U_α = Information relating to thermodynamics in the section. The fluctuation of information among sections should be dictated by the equations for a <u>canonical ensemble.</u>

8.2 To maximize q_j (or $\ln q$) under the constraint $\sum_i N_{ij} = N_j$

$$q_j \equiv \prod_i \frac{g_i^{N_{ij}}}{N_{ij}!} \exp\left(-\sum_i N_{ij}\epsilon_i/kT\right)$$

Subscript j can be dropped here.

$$d \ln q_i = d \sum_i \left[N_i \ln g_i - N_i \ln N_i + N_i - \sum_i N_i \epsilon_i / kT\right]$$

$$= \sum_i \left[\ln g_i - \ln N_i - \frac{\epsilon_i}{kT}\right] dN_i = 0 \qquad (A)$$

$$d\left(\sum N_i\right) = dN = 0 \ , \quad \sum_i \alpha \, dN_i = 0 \ (B)$$ α: Lagrangian multiplier

$$(A)+(B) \rightarrow \sum_i \left[\ln g_i - \ln N_i - \frac{\epsilon_i}{kT} + \alpha\right] dN_i = 0$$

(The second Lagrangian multiplier β is not needed because of only one contraint)

$$N_i = e^{\alpha} g_i e^{-\epsilon_i/kT}$$

$$\sum N_i = N \longrightarrow N_i = \frac{N g_i e^{-\epsilon_i/kT}}{\sum_i g_i e^{-\epsilon_i/kT}} \qquad (c)$$

8.2 (continued)

Substituting (c) into

$$\ln q = \sum_i \left[N_i \ln g_i - N_i \ln N_i + N_i - N_i \epsilon_i / kT \right]$$

$$= \sum_i \left[N_i \ln g_i - N_i \ln\left(\frac{N}{Z} g_i e^{-\epsilon_i/kT} \right) + N_i - N_i \epsilon_i / kT \right]$$

$$= \sum_i \left[N_i - N_i \ln N + N_i \ln Z \right] = N - N \ln N + N \ln Z$$

$$= \ln \left[\frac{e}{N} Z \right]^N$$

8.3

$$G_{jk\ell} = \prod_i \frac{g_{ai}^{(N_{ai})_{jk\ell}} \; g_{bi}^{(N_{bi})_{jk\ell}}}{(N_{ai})_{jk\ell}! \; (N_{bi})_{jk\ell}!} \qquad \underline{\text{compare with}} \; \text{Eq. (8.36)}$$

$$\sum_i (N_{ai})_{jk\ell} = N_{aj} \, , \quad \sum_i (N_{bi})_{jk\ell} = N_{b\ell} \qquad \text{Eq. (8.37)}$$

$$\sum_i \left[(N_{ai})_{jk\ell} \epsilon_{ai} + (N_{bi})_{jk\ell} \epsilon_{bi} \right] = U_k \qquad \text{Eq (8.38)}$$

$$\frac{\tilde{N}_{jk\ell}}{\tilde{N}} = \frac{G_{jk\ell} \exp(-\alpha_a N_{aj} - \alpha_b N_{b\ell} - \beta U_k)}{\sum_j \sum_k \sum_\ell G_{jk\ell} \exp(-\alpha_a N_{aj} - \alpha_b N_{bj} - \beta U_k)} \qquad \text{Eq. (8.39)}$$

$$\frac{\tilde{N}_{jk\ell}}{\tilde{N}} = \frac{G_{jk\ell} \exp\left[(\mu_a N_{aj} + \mu_b N_{b\ell} - U_k)/kT \right]}{\sum_j \sum_k \sum_\ell G_{jk\ell} \exp\left[(\mu_a N_{aj} + \mu_b N_{b\ell} - U_k)/kT \right]} \qquad \text{Eq. (8.41)}$$

8.4 1.) $U = U(S, V, N)$ Eq. (1.5)

$$\Psi = U - \left(\frac{\partial U}{\partial S} \right)_{V,N} S - \left(\frac{\partial U}{\partial N} \right)_{S,V} N = U - TS - \mu N = \Psi(T, V, \mu)$$

From Euler eqn. [Eq. (1.32)] $\Psi(T,V,\mu) = -[PV](T,V,\mu)$

Thus Eq. (8.46) — $PV(T,V,\mu) = kT \ln Q_G(T,V,\mu)$ is a fundamental equation. (Compare with Example 1.3)

8.4 (Continued)

2.) $-(pV) = U - TS - \mu N$

$$d(pV) = -dU + TdS + SdT + \mu dN + Nd\mu$$
$$= SdT + pdV + Nd\mu \qquad (\because dU = TdS - pdV + \mu dN)$$

Eqs. (8.47), (8.48), (8.49) and (8.50) follow directly.

8.5
$$\psi\left[\tfrac{1}{T}, \tfrac{p}{T}, N\right] = S - \frac{U}{T} - \frac{pV}{T} = \underbrace{-\frac{G}{T}\left(\tfrac{1}{T}, \tfrac{p}{T}, N\right)}_{\text{macroscopic governing parameter}}$$

$$Q_g\left(\tfrac{1}{T}, \tfrac{p}{T}, N\right) = \underline{\underline{\sum_i \sum_j G_{ij} \exp\left[-(U_i + pV_j)/kT\right]}}$$

Q_g: microscopic governing parameter

$$-\frac{G}{T}\left(\tfrac{1}{T}, \tfrac{p}{T}, N\right) = k \ln Q_g\left(\tfrac{1}{T}, \tfrac{p}{T}, N\right)$$ governing relation

8.6
$$\bar{U} = \sum_j P_j U_j \quad , \quad \bar{p} = \sum_j P_j p_j$$

where $P_j = G_j e^{-\beta U_j(V,N)} / Q$ see Eq. (8.12a) & (8.16)

$$p_j = -\left(\frac{\partial U_j}{\partial V}\right)_N$$

$$\left(\frac{\partial \bar{U}}{\partial V}\right)_{\beta,N} = \sum_j \left(\frac{\partial P_j}{\partial V}\right)_{\beta,N} U_j + \sum \left(\frac{\partial U_j}{\partial V}\right)_{\beta,N} P_j$$

$$\left(\frac{\partial P_j}{\partial V}\right)_{\beta,N} = P_j\left[-\beta\left(\frac{\partial U_j}{\partial V}\right)_N - \left(\frac{\partial \ln Q}{\partial V}\right)_{\beta,N}\right]$$

$$\sum_j U_j \left(\frac{\partial P_j}{\partial V}\right)_{\beta,N} = \sum_j P_j U_j \left[-\beta\left(\frac{\partial U_j}{\partial V}\right) - \left(\frac{\partial \ln Q}{\partial V}\right)\right] = \sum_j P_j U_j \left[\beta p_j - \beta \bar{p}\right]$$

$$\left(\frac{\partial \bar{U}}{\partial V}\right)_{\beta,N} = \sum_j P_j U_j \beta p_j - \beta \bar{p} \bar{U} - \bar{p}$$

Similarly, $\left(\frac{\partial \bar{p}}{\partial \beta}\right)_{V,N} = \sum p_j \left(\frac{\partial P_j}{\partial \beta}\right)_{V,N} + \sum P_j \cancelto{0}{\left(\frac{\partial p_j}{\partial \beta}\right)_{V,N}}$

$$= \sum_j p_j P_j \left[-U_j - \left(\frac{\partial \ln Q}{\partial \beta}\right)_{V,N}\right] = -\sum P_j U_j p_j + \bar{U}\bar{p}$$

Thus. $\left(\frac{\partial \bar{U}}{\partial V}\right)_{\beta,N} + \beta\left(\frac{\partial \bar{p}}{\partial \beta}\right)_{V,N} = -\bar{p}$

8.7

$$S = -\sum_i P_i \ln P_i \qquad P_i = \frac{G_i e^{-\beta U_i}}{Q}$$

$$dS = 0 = -\sum_i dP_i - \sum_i \ln P_i \, dP_i$$

$$\sum_i dP_i = 0$$

$$\sum_i [-1 - \ln P_i + \alpha] dP_i = 0 \qquad \alpha: \text{Lagrangian multiplier}$$

$$P_i = e^{\alpha - 1} = \text{constant}$$

8.8

$$S(U,V,N) = k \ln \Omega (U,V,N)$$

Since $\displaystyle S = \underbrace{\tfrac{1}{T}}_{\left(\frac{\partial S}{\partial U}\right)} U + \underbrace{\tfrac{p}{T}}_{\left(\frac{\partial S}{\partial V}\right)} V - \underbrace{\tfrac{\mu}{T}}_{\left(\frac{\partial S}{\partial N}\right)} N$ Eq. (1.33)

Eq. (1.7)

$$\ln \Omega = U\left(\frac{\partial \ln \Omega}{\partial U}\right) + V\left(\frac{\partial \ln \Omega}{\partial V}\right) + N\left(\frac{\partial \ln \Omega}{\partial N}\right)$$

8.9

$$C_v = T\left(\frac{\partial S}{\partial T}\right)_{V,N} = kT^2\left(\frac{\partial^2 \ln Q}{\partial T^2}\right) + 2kT\left(\frac{\partial \ln Q}{\partial T}\right) = \frac{\partial}{\partial T}\left(kT^2 \frac{\partial \ln Q}{\partial T}\right)$$

$$\left(\because \quad S = -\left(\frac{\partial F}{\partial T}\right)_{V,N}, \quad F = -kT \ln Q \right)$$

$$kT^2 \frac{\partial \ln Q}{\partial T} = \int_0^T C_v \, dT + C_1 \qquad C_1 = 0 \text{ because of } T \to 0 \text{ behavior}$$

$$\ln Q = \int_0^T \left[\frac{1}{kT^2} \int_0^T C_v \, dT\right] dT + C_2$$

(C_2 is non-zero because of zero-point energy of vibration in solids at $0°K$)

8.10

$$\frac{\sigma_p}{\bar{p}} \approx \frac{1}{\sqrt{N}} \qquad \text{Eq. (8.55)} \qquad \text{(Note: valid under ideal-gas assumption)}$$

Consider 1% fluctuation as noticeable: $\frac{1}{\sqrt{N}} \approx 0.01 \quad N \approx 10^4$

$$\rho_{air} = \frac{N \cdot M}{V} = \frac{10^4 (29/6 \times 10^{23})}{1} \; \frac{6.85 \times 10^{-5}}{5.787 \times 10^{-4}} = 5.73 \times 10^{-20} \frac{slug}{ft^3}$$

Compare with sea level, $\rho_{air} = 0.0023 \frac{slug}{ft^3}$; $h = 2.6 \times 10^5$ ft, $\rho = 10^{-7}$ slug/ft^3

(see, for instance, Table B.1. in Shapiro "The Dynamics and Thermodynamics of Compressible Fluid Flow, Vol. I")

8.11 A given plate is one sample system out of a large ensemble of systems whose average number of sites is N_0. We have seen (§8.5) that for a variety of variables with Gaussian distribution functions, $\sigma_N/N_0 = 1/\sqrt{N_0}$. We would expect N to be a Gaussian variable as well. If we stay outside the 2-σ limits, then 95% of the samples will fall within the prescribed error. Therefore:

$$\sigma_N = \sqrt{N_0} \quad \text{or} \quad \sigma_n = \frac{\sqrt{N_0}}{A} = \sqrt{\frac{n_0}{A}}$$

& we want $\frac{2\sigma_n}{n_0} < 0.03$ or $\frac{2}{\sqrt{n_0 A}} < 0.03$. But $A = \frac{1}{14.4}\,ft^2$ so $n > \frac{(66.7)^2}{1/14.4} = 64{,}000$ sites/ft². Thus are asking for more accuracy than is reasonable to expect. 20% would have been more reasonable.

8.12 $$\overline{\Delta U^3} = \overline{(U-\bar{U})^3} = \overline{U^3} - 3\overline{U^2}\,\bar{U} + 3\bar{U}\,\bar{U}^2 - \bar{U}^3 = \overline{U^3} - 3\overline{U^2}\bar{U} + 2\bar{U}^3$$

Since $Q = \sum G_i e^{-\beta U_i}$ $\quad \frac{\partial Q}{\partial \beta} = \sum -U_i G_i e^{-\beta U_i} = -\bar{U} Q$

$$\frac{\partial^2 Q}{\partial \beta^2} = \sum U_i^2 e^{-\beta U_i} = Q\,\overline{U^2}, \quad \frac{\partial^3 Q}{\partial \beta^3} = -Q\,\overline{U^3}$$

$$\frac{\partial^3 \ln Q}{\partial \beta^3} = \frac{\partial^2}{\partial \beta^2}\left(\frac{1}{Q}\frac{\partial Q}{\partial \beta}\right) = \frac{\partial}{\partial \beta}\left[\frac{1}{Q}\frac{\partial^2 Q}{\partial \beta^2} - \frac{1}{Q^2}\left(\frac{\partial Q}{\partial \beta}\right)^2\right]$$

$$= \frac{1}{Q}\frac{\partial^3 Q}{\partial \beta^3} - \frac{3}{Q^2}\left(\frac{\partial Q}{\partial \beta}\right)\left(\frac{\partial^2 Q}{\partial \beta^2}\right) + \frac{2}{Q}\left(\frac{\partial Q}{\partial \beta}\right)^3 = -\overline{\Delta U^3}$$

8.13 $$\bar{U} = \sum_i N_i \epsilon_i \qquad N_i = \frac{N}{Z} g_i e^{-\epsilon_i/kT}$$

$$d\bar{U} = C_v\,dT = \sum_i \epsilon_i \left(\frac{\partial N_i}{\partial T}\right) dT \qquad [\because \epsilon_i = \epsilon_i(V)]$$

$$= \sum_i \epsilon_i N_i \frac{(\epsilon_i - \bar{\epsilon})}{kT^2}\,dT = \sum_i \frac{\epsilon_i(\epsilon_i - \bar{\epsilon})}{kT^2 Z} N g_i e^{-\epsilon_i/kT}\,dT$$

$$\frac{kT^2}{N} C_v = \sum_i \left[\epsilon_i^2 \frac{g_i}{Z} e^{-\epsilon_i/kT} - \bar{\epsilon}\epsilon_i \frac{g_i}{Z} e^{-\epsilon_i/kT}\right]$$

$$C_V = \frac{N}{kT^2}\left(\overline{\epsilon^2} - \bar{\epsilon}^2\right)$$

8.14 $\overline{U^2} - \overline{U}^2 = \sigma_U^2 = kT^2 C_v$ Eqs. (8.51) and (8.53)

$\overline{\epsilon^2} - \overline{\epsilon}^2 = \sigma_\epsilon^2 = kT^2 C_v/N$ (Prob. 8.13)

$\sigma_\epsilon^2 N = \sigma_U^2 \qquad \frac{\sigma_\epsilon}{\overline{\epsilon}} = N^{\frac{1}{2}} \frac{\sigma_U}{\overline{U}}$

8.15 From Eq. (8.39) $\mathcal{P}(N_i, U_k) = \frac{\tilde{N}_{ik}}{\tilde{N}} = \frac{G_{ik} \exp(-\alpha N_i - \beta U_k)}{Q_G}$

$$\mathcal{P}(N_i) = \sum_k \mathcal{P}(N_i, U_k) = \sum_k \frac{G_{ik}}{Q_G} e^{-\alpha N_i - \beta U_k} = \frac{e^{-\alpha N_i}}{Q_G} \sum_k G_{ik} e^{-\beta U_k}$$

$$= \frac{e^{-\alpha N_i}}{Q_G} \frac{1}{N_i!\, h^{3N_i}} \int e^{-U(\vec{r}_j, \vec{p}_j)/kT} \prod_j^{N_i} d\vec{r}_j\, d\vec{p}_j \quad \left[\begin{array}{l}\text{see Eq. (5.37)} \\ \text{and Eq. (7.2) for } N!\end{array}\right]$$

$$= \frac{e^{-\alpha N_i}}{Q_G} \frac{Z^{N_i}}{N_i!} \quad \left(\text{because of ideal gases } U = \sum_i \epsilon_i\right)$$

Since $PV = kT \ln Q_G$, $\ln Q_G = \frac{PV}{kT} = N$, $Q_G = e^N$

$F = -NkT \ln\left(\frac{Ze}{N}\right)$, $\left(\frac{Ze}{N}\right) = e^{-F/NkT} = e^{-(G-PV)/NkT} = e \cdot e^{-\mu/kT}$

$$\mathcal{P}(N_i) = \frac{e^{\mu N_i/kT}}{e^N} \frac{1}{N_i!} \left(N e^{-\mu/kT}\right)^{N_i}$$

$$= \frac{1}{N_i!} e^{-N} N^{N_i}$$

CHAPTER 9

9.1 From Eq. (8.31) $Q = \frac{Z^N}{N!} \simeq \left(\frac{Ze}{N}\right)^N$

or $Q = Q_{int} \frac{1}{N!} Z_{tr}^{\,N}$ but now Z_{tr} includes the hybrid translational and intermolecular potential energies as given by Eq. (9.1). Finally Z_{tr} is given by the phase integral Eq. (5.26), but over 3N coördinates instead of just 3 coordinates. The result is Eq. (9.2).

9.2 $$Z_\Phi = \int \cdots \int \exp(-0)\, d\vec{r}_1 \cdots d\vec{r}_N = V^N$$

Then $F = -NkT[\underbrace{\ln Z_{int}}_{0} - \ln N + 1 - 3\ln\Lambda] - kT\ln V^N$

and $$p = -\left.\frac{\partial F}{\partial V}\right|_{T,N} = \frac{kTN}{V} = \underline{\underline{\frac{R^\circ T}{v}}}$$

9.3 we have: (at the critical point)

$$\left.\begin{aligned} p_c &= \frac{R^\circ T_c}{v_c - b} - \frac{a}{v_c^2} \\ 0 &= -\frac{R^\circ T_c}{(v_c-b)^2} + \frac{2a}{v_c^3} \\ 0 &= \frac{R^\circ T_c}{(v_c-b)^3} - \frac{6a}{v_c^4} \end{aligned}\right\}$$

solving these simultaneously for a, b and R° we obtain:

Eq. (9.31) $\underline{a = 3 p_c v_c^2}$

Eq. (9.32) $\underline{b = v_c / 3}$

Eq. (9.33) $\underline{R^\circ = \frac{8}{3}\frac{p_c v_c}{T_c}}$

Then put these in the vander Waals Equation:

$$p = \frac{\frac{8}{3}\frac{p_c v_c}{T_c} \cdot T}{v - \frac{v_c}{3}} - \frac{3 p_c v_c^2}{v^2}$$

so $$\underline{p_r = \frac{8 T_r}{3 v_r - 1} - \frac{3}{v_r^2}}$$

9.4 This problem is solved in different ways in many classical thermodynamics texts. We would refer to: H.B. Callen, <u>Thermodynamics</u>, John Wiley & Sons, 1961, Sec. 8.1; or to J.H. Keenan, <u>Thermodynamics</u>, John Wiley & Sons, 1954, Ch XXIII and Ch XXIV.

9.5 $$p_r = \frac{8T_r}{3v_r - 1} - \frac{3}{v_r^2} \quad ; \quad \left.\frac{\partial p_r}{\partial v_r}\right|_{v_{r_m}} = 0 = \left[-\frac{3 \cdot 8 T_r}{(3v_r - 1)^2} + \frac{6}{v_r^3} \right]_{v_r = v_{r_m}}$$

$$\text{so} \quad \frac{8T_r}{3v_{r_m} - 1} = \frac{2(3v_{r_m} - 1)}{v_{r_m}^3} \quad \& \quad \underline{\underline{p_r = \frac{1}{v_{r_m}^2}\left[3 - \frac{2}{v_{r_m}}\right]}}$$

9.6 for a single component fluid $d\mu = dg = v\,dp - s\,dT$ and along a const. temp. path $dT = 0$ so $\underline{g_g - g_f = 0 = \int v\,dp}$

$$\frac{\partial}{\partial p}(c_p) = \frac{\partial}{\partial p}\left(T \frac{\partial s}{\partial T}\right) = T\frac{\partial^2 s}{\partial p\,\partial T} = T\frac{\partial}{\partial T}\left(\frac{\partial s}{\partial p}\right) = T\frac{\partial}{\partial T}\left(\frac{\partial v}{\partial T}\right) = T\frac{\partial^2 v}{\partial T^2}$$

$$\text{so:} \quad \underline{c_p(T, p) = c_p^0(T) + \int_0^p T\frac{\partial^2 v}{\partial T^2}\,dp}$$

9.7 from Eq. (9.6) $$Z_\phi = \int_0^\sigma \cdots \int 0 \, d\vec{r}_1 \cdots d\vec{r}_N + \int_\sigma^\infty \cdots \int 1 \, d\vec{r}_1 \cdots d\vec{r}_N \neq f(T)$$

$$\text{so} \quad p = -\frac{\partial F}{\partial V} = kT\frac{\partial Z_\phi}{\partial V} \quad \text{or} \quad \underline{\frac{p}{R^\circ T} = \frac{1}{N_A}\frac{\partial Z_\phi}{\partial V} \neq f(T)}$$

Hence no virial coeffs. depend on T

9.8 $$B(T) = 2\pi N_A \left(\int_0^\sigma (1 - 0) r^2 dr + 2\pi N_A \int_\sigma^\infty \left(1 - \exp\left[+\frac{c}{kTr^\delta}\right]\right) r^2 dr \right.$$

$$= 2\pi N_A (\sigma^3/3) - 2\pi N_A \int_\sigma^\infty \sum_{j=1}^\infty \frac{1}{j!}\left(\frac{c}{kTr^\delta}\right)^j r^2 dr = b + 2\pi N_A \sum_{j=1}^\infty \left(\frac{c}{kTr^\delta}\right)^j \frac{r^3}{j!(j\delta - 3)}\Bigg]_\sigma^\infty$$

$$\underline{B(T) = b\left[1 + \sum_{j=1}^\infty \frac{3}{j!(j\delta - 3)}\left(\frac{c}{\sigma^\delta kT}\right)^j\right]}$$

9.9 $b_{vdw} = \frac{v_c}{3} = \frac{1}{3}\,\frac{3}{8}\,\frac{R^\circ T_c}{p_c} = \frac{R^\circ}{8}\,\frac{T_c}{p_c} = 10.257\,\frac{\text{atm cm}^3}{{}^\circ K}\,\frac{T_c}{p_c}$

This is 44% of the empirical value -- Eq. (9.55)

9.10 A rigorous formulation of the combined effects of an intermolecular force field and a gravitational field would be very complex. However the molecular field involves distances of microscopic size while the gravity field involves distances of macroscopic size. Thus we can effectively separate the two effects.

$$F(T,V,N) = -kT \ln Q(T,V,N) = -kT \ln \sum_j G_j \exp(-U_j/kT)$$

where $U_j = \sum_i \frac{\vec{p}_i^{\,2}}{2m} + \sum_i mgz_i + \phi$, so

$$F = -kT \ln \left[(2m\pi kT)^{3/2} \frac{kT}{mg} \frac{1}{L} \left(\frac{e}{N}\right) \frac{1}{h^3} \right]^{N_A} Z_\phi$$

where L is a constant with the units of length, and

$$Z_\phi = V^{N_A}\left[1 - \frac{N_A B(T)}{V} + \cdots\right]$$

We know that B = const for the hard sphere model.

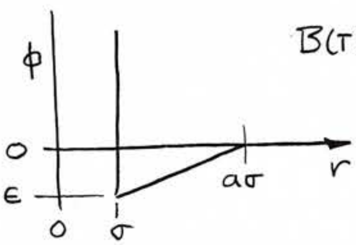
Then: $$U = kT^2 \frac{\partial \ln Q}{\partial T}\bigg|_{V,N} = \frac{5}{2} R^\circ T; \qquad \underline{\underline{c_v = \frac{5}{2} R^\circ}}$$

This is the same result as we obtained in Example 3.2 -- There is no effect from the rigid sphere behavior.

AND $$p = -\frac{\partial F}{\partial V} = kT \frac{\partial \ln Z_\phi}{\partial V}, \quad \text{so} \quad \underline{\underline{\frac{pv}{R^\circ T} = 1 + \frac{B}{v}}}$$

This is Eq. (9.22). There is no effect from the gravity field, on the local pressure.

9.11



$$B(T) = 2\pi N_A \int_0^{\sigma} (1-0) r^2 dr + 2\pi N_A \int_{\sigma}^{a\sigma} \left(1 - \exp\left[-\frac{\epsilon(r-a\sigma)}{kT\sigma(a-1)}\right]\right) r^2 dr + 0$$

$$= b + 2\pi N_A \int_{\sigma}^{a\sigma} \sum_{i=1}^{\infty} \frac{1}{i!}\left(\frac{-\epsilon}{kT\sigma(a-1)}\right)^i (r-a\sigma)^i r^2 dr$$

$$B(T) = b\left\{1 + \frac{3}{\sigma^3}\sum_{i=1}^{\infty}\frac{(-1)^i}{i!}\left(\frac{\epsilon}{kT\sigma(a-1)}\right)^i \left[\frac{(r-a\sigma)^{i+3}}{i+3} + \frac{2a\sigma(r-a\sigma)^{i+2}}{i+2} + \frac{a^2\sigma^2(r-a\sigma)^{i+1}}{i+1}\right]_{\sigma}^{a\sigma}\right\}$$

$$\underline{B(T) = b\left\{1 + 3\sum_{i=1}^{\infty}\frac{1}{i!}\left(\frac{\epsilon}{kT}\right)^i\left[\frac{(a-1)^3}{i+3} - \frac{2a(a-1)^2}{i+2} + \frac{a^2(a-1)}{i+1}\right]\right\}}$$

Check: for $\epsilon \ll kT$ we need only keep the first term

$$B(T) = b\left(1 + \frac{\epsilon a^3}{4kT}\cdot\frac{12}{a^3}\left[\frac{(a-1)^3}{4} - \frac{2a(a-1)^2}{3} + \frac{a^2(a-1)}{2}\right]\right)$$

$$= b\left(1 - \frac{\epsilon a^3}{4kT}\left[1 + \frac{1}{a} + \frac{1}{a^2} + \frac{1}{a^3}\right]\right) \simeq b\left(1 - \frac{\epsilon a^3}{4kT}\frac{a}{a-1}\right)$$

alternatively:

$$B(T) \simeq b + 2\pi N_A \int_{\sigma}^{a\sigma} \frac{-\epsilon}{kT\sigma(a-1)}\cdot(r-a\sigma) r^2 dr$$

$$= b + 2\pi N_A \frac{\epsilon}{kT\sigma(a-1)}\left(\frac{(a\sigma)^4 - \sigma^4}{4} - \frac{a^4\sigma^4 - a\sigma^4}{3}\right)$$

$$= b\left(1 + \frac{\epsilon a^3}{4kT}\left[\frac{a}{a-1}\right]\underbrace{\left[-1 - \frac{3}{a^3} + \frac{4}{a^4}\right]}_{\simeq -1}\right)$$ about the same.

9.12 from Example 9.3, $\mu = \frac{b}{c_p}\left[\frac{\partial B^*}{\partial \ln T^*} - B^*\right]$

where: $B^* = 1 - (1.85^3 - 1)\left[\exp\left(\frac{1}{T^*}\right) - 1\right]$

$$\frac{\partial B^*}{\partial \ln T^*} = + \frac{5.34\exp\left(\frac{1}{T^*}\right)}{T^*}$$

and $\frac{b}{c_p} = \frac{50\times 2}{5\times 8.3143\times 10^7} = 2.4\times 10^{-7}\ \frac{{}^\circ C\ cm^2}{dyne}$

$c_p \simeq \frac{5}{2}R^\circ$

$b = 2\pi N_A \frac{\sigma^3}{3}$

$\sigma = 3.41\times 10^{-8}$

$b = 50$

9.12 cont'd.) $\mu = 2.4\times10^{-7}\left[+\frac{5.34}{T^*}\exp\left(\frac{1}{T^*}\right) - 1 - 5.34 + \frac{5.34}{T^*}\exp\left(\frac{1}{T^*}\right)\right]$

$$\underline{\mu = -1.52\times10^{-6}\ {}^\circ C/\text{dyne/cm}^2} \neq f(T^*)$$
$$\neq f(\text{Argon})$$

9.13 $Z_\phi = V^{N_1+N_2}\left[1 - \frac{N_1^2 B_{1,1}}{N_A V} - \frac{N_2^2 B_{2,2}}{N_A V} - \frac{N_1 N_2 B_{1,2}}{N_A V}\right]$

$$p = \frac{\partial F}{\partial V} = +kT\frac{\partial \ln Z_\phi}{\partial V} = kT\frac{\partial}{\partial V}\ln\left[V^{N_1+N_2}\left(1 - \frac{N_1^2 B_{1,1}}{N_A V} - \cdots\right)\right]$$

$$= \frac{(N_1+N_2)kT}{V}\left[1 + \underbrace{\frac{x_1^2}{V}B_{1,1} + \frac{x_2^2}{V}B_{2,2} + \frac{x_1x_2}{V}B_{1,2}}\right]$$

so $B_{effective} \simeq \sum_{i,j=1}^{2} x_i x_j B_{i,j}$

9.14 For a mixture : $F(T,V,N_1,\cdots,N_r) = -kT\ln Q(T,V,N_1,\cdots,N_r)$

$$Q = \left[\prod_j^r (z_{int_j})^{N_j}\frac{1}{N_j!}\Lambda_j^{-3N_j}\right]Z_\phi \qquad [\text{see Eq.}(9.5)]$$

$$Z_\phi = V^{\sum_j N_j}\left[1 - \frac{(\sum N_j)B(T)}{V} + \cdots\right] \quad B(T) = \sum_i\sum_k x_i x_k B_{ik}(T) \quad [\text{see Eq.}(9.60)]$$

For a binary mixture : $B(T) = x_1^2 B_{11} + x_1x_2 B_{12} + x_2^2 B_{22}$

For an isentropic expansion : $dS = 0$ (but ds_j may not be zero)

$$S = -\left(\frac{\partial F}{\partial T}\right)_{V,N}, \quad dS = -\left(\frac{\partial^2 F}{\partial T^2}\right)_{V,N}dT - \left(\frac{\partial^2 F}{\partial T\partial V}\right)dV \quad (F \text{ given above})$$

(a) z_{int} for the monoatomic component is zero. $B(T) = 0$

$$Z_\phi = V^{N_1+N_2} = V^{N_1}V^{N_2}$$

(b) Rigid sphere case : There exist three kinds of interactions:

$$B_{11} = \frac{2\pi N_1}{3}\sigma_1^3, \quad B_{12} = \frac{2\pi}{3}\left(\frac{N_1+N_2}{2}\right)\left(\frac{\sigma_1+\sigma_2}{2}\right)^3, \quad B_{22} = \frac{2\pi N_2}{3}\sigma_2^3$$

(c) L-J case : Three kinds of interactions characterized by

σ_1, ϵ_1; $\sigma_1 (=\sigma_2)$, $2\epsilon_1/k$; and $\sigma_1 \left(=\frac{\sigma_1+\sigma_2}{2}\right)$, $\sqrt{2}\epsilon_1/k$

9.15 $p_a = 500$ psia $\quad T_a = 68°C = 154°F = 614°R$

$(T_c)_a = 238.8°R \qquad (T_r)_a = \frac{T_a}{(T_c)_a} = 2.58 = (T_r)_s$

$(p_c)_a = 547$ psia $\qquad (p_r)_a = \frac{p_a}{(p_c)_a} = 0.915 = (p_r)_s$

$T_s = (T_r)_s\,(T_c)_s = 2.58 \times 1165.4 = 2990°R = 2530°F$

$p_s = (p_r)_s\,(p_c)_s = 0.915 \times 3260 = 2980$ psia

From steam table: $\quad v_s = 0.578\ ft^3/lbm$

$(v_r)_s = \frac{v_s}{(v_c)_s} = \frac{0.578}{0.0503} = 11.5 = (v_r)_a$

$v_a = (v_r)_a\,(v_c)_a = 11.5 \times 0.046 = \underline{0.528\ ft^3/lbm}$

(a) Use Z-Chart:

$(p_r)_a = 0.915, \quad (T_r)_a = 2.57, \quad Z \approx 1.0$ (like ideal gas)

$v = \frac{ZRT}{p} = \frac{1(53.35)\times 614}{500 \times 144} = \underline{0.455\ ft^3/lbm}$

(c) Use air table:

$T = 238.8°R, \quad p_{r_1} = 0.08, \quad v_{r_1} = 110$

$p_{r_2} = \frac{500}{547} \times 0.08 = 0.0731, \quad T_2 \approx 233°R, \quad v_{r_2} = 1180$

$v_2 = \frac{v_{r_2}}{v_{r_1}} \times v_1 = \frac{1180}{110} \times 0.046 = \underline{0.494\ ft^3/lbm}$

9.16 $(p + \frac{a}{v^2})(v - b) = RT \qquad \frac{pv}{RT} = \frac{1}{(1+\frac{a}{pv^2})(1-\frac{b}{v})}$

For p (or p_r) large, $\frac{a}{pv^2} \ll 1$, $Z = \frac{pv}{RT} > 1$

$Z \gg 1$ when p large, v small, or T in moderate range.

9.17 $T_1 = 800°F = 1260°R \qquad p_1 = 1000$ psia

$p_{r_1} = \frac{1000}{3210} = 0.312, \qquad T_{r_1} = \frac{1260}{1165.4} = 1.08$

From defect chart, $\quad \left(\frac{H^* - H}{T_c}\right)_1 = 0.59$ Btu/lbm-mole·°R

9.17 (Continued)

$$h_1 - h_2 = \int_2^1 c_p\,dT - (h^* - h)_1 + (h^* - h)_2$$

For Joule - Thomson expansion, $h_1 = h_2$

$$0 = \int_{T_2}^{T_1} (0.433 + 0.0000166T)\,dT - \left(\frac{H^* - H}{T_C}\right)\frac{T_c}{M} + \underbrace{\cancel{(h^* - h_2)}}_{\text{negligible} \to 0}$$

$$0 = 0.433(1260 - T_2) + 0.0000083(1260^2 - T_2^2) - 38.2$$

$$0.0000083\,T_2^2 + 0.433\,T_2 - 525.1 = 0$$

$$T_2 \approx 1145°R = \underline{685°F} \qquad \left(\begin{array}{l}\text{From steam chart} \\ T_2 \approx 700°F\end{array}\right)$$

9.18 From Eq. (9.18) $\quad p = kT\dfrac{\partial \ln Z_\phi(T,V)}{\partial V} = \dfrac{kTN_A}{b}\cdot\dfrac{\partial \ln Z_\phi}{\partial v^*}$

From the form of Eq. (9.6) for Z_ϕ, $\quad Z_\phi = Z_\phi(T^*, v^*)$

$$p = \frac{kTN_A}{b} f_1(v^*, T^*) \qquad \frac{pb}{\epsilon N_A} = \frac{kT}{\epsilon} f_1(v^*, T^*)$$

$$p^* = T^* f_1(v^*, T^*) = f(v^*, T^*)$$

(Or, from dimensional analysis about the parameters, $p, v, T, \epsilon, \sigma$.)

9.19 $\quad F(T,A,N) = -kT\ln Q(T,A,N)$

$$Q(T,A,N) = \left[\frac{e}{N}\left(\frac{2\pi mkT}{h^2}\right)\right]^N Z_{int}^N\, Z_\phi(T,A,N)$$

$$Z_\phi = A^N + A^{N-1}\frac{N(N-1)}{2}\int_0^\infty 2\pi r\,\phi(r)\,dr$$

Chapter 10

10.1 $$F = -kT \ln\left[e^{-N\phi/2kT} Z^{3N}\right] \qquad \text{Eq. } (10.5)$$

$$C_v = \left(\frac{\partial U}{\partial T}\right)_{V,N} = -T\left(\frac{\partial^2 F}{\partial T^2}\right)_{V,N} = 6NkT\frac{\partial \ln Z}{\partial T} + 3NkT^2\frac{\partial^2 \ln Z}{\partial T^2} \qquad (A)$$

$$\ln Z = \ln\left[\frac{e^{-\theta/2T}}{1-e^{-\theta/T}}\right] = \ln\left[\frac{e^{\theta/2T}}{e^{\theta/T}-1}\right] = \frac{\theta}{2T} - \ln\left[e^{\theta/T}-1\right]$$

$$\frac{\partial \ln Z}{\partial T} = -\frac{\theta}{2T^2} + \frac{\frac{\theta}{T^2}e^{\theta/T}}{\left[e^{\theta/T}-1\right]}$$

$$\frac{\partial^2 \ln Z}{\partial T^2} = \frac{\theta}{T^3} + \left[\left(e^{\theta/T}-1\right)\left(-\frac{2\theta}{T^3}e^{\theta/T} - \frac{\theta^2}{T^4}e^{\theta/T}\right) + \frac{\theta^2}{T^4}e^{2\theta/T}\right]\left[e^{\theta/T}-1\right]^{-2}$$

Substituting into (A) gives $\quad C_v = 3Nk\left(\frac{\theta}{T}\right)^2 \frac{\exp(\theta/T)}{\left[\exp(\theta/T)-1\right]^2} \quad$ Eq.(10.6)

$$\lim_{T\to\infty} C_v = 3Nk \lim_{T\to\infty} \frac{\left(\theta/T\right)^2}{\left[1+(\theta/T)+\cdots-1\right]^2} = 3Nk \qquad \text{Eq. }(10.7)$$

$$\lim_{T\to 0} C_v = 3Nk\, \frac{(\theta/T)^2 \exp(\theta/T)}{\left[\exp(\theta/T)\right]^2} = 3Nk\left(\frac{\theta}{T}\right)^2 \exp\left(-\frac{\theta}{T}\right) \quad \text{Eq.}(10.8)$$

10.2 For sound waves $\quad g(\nu) = \frac{4\pi V}{c^3}\nu^2 \quad$ see Eq.(10.14)

total no. of modes $= \int_0^{c/\ell} g(\nu)\, d\nu = \frac{4\pi V}{3\ell^3}$

no. of translation modes $= 3N - \frac{4\pi V}{3\ell^3}$

Since $\frac{4\pi V}{3\ell^3} << 3N \qquad \left[\because \ell \sim 10^2\left(\frac{V}{N}\right)^{1/3}\right]$

We could use $3N$ for translational modes.

$$Q = \underbrace{\left(Z_{int}\right)^N \frac{1}{N!}\Lambda^{-3N} Z_\phi}_{Q_t} \prod_i^{\left(\frac{4\pi V}{3\ell^3}\right)} q_{sound} \qquad (\text{see Eq. } (9.5))$$

$$\ln Q = \ln Q_t - \int_0^{\left(\frac{4\pi V}{3\ell^3}\right)} \left[\ln\left(1-e^{-h\nu/kT}\right) + \frac{h\nu}{2kT}\right]\left(\frac{4\pi V}{c^3}\nu^2\right) d\nu$$

$$F = -kT\ln Q \qquad U = kT^2\left(\frac{\partial \ln Q}{\partial T}\right)_{V,N}.$$

10.3 $\mu_{solid} = \mu_{vapor}$

$$\mu_{solid} = \left(\frac{\partial F_{solid}}{\partial N}\right)_{T,V} = \frac{\phi}{2} - 3kT\ln\left(\frac{e^{-\theta/T}}{1-e^{-\theta/T}}\right) \quad \text{(use Eq(10.5))}$$

$$\mu_{gas} = \left(\frac{\partial F_{gas}}{\partial N}\right)_{V,T} = -T\left(\frac{\partial S_{gas}}{\partial N}\right) = -kT\left\{\ln\left[\left(\frac{2\pi mkT}{h^2}\right)^{3/2}\frac{kT}{p_0}\right] + \frac{5}{2}\right\}$$

(use Eq. (7.15a))

$$\ln p_0 = \frac{5}{2} + \frac{5}{2}\ln T + \frac{\phi(0)}{2kT} - 3\ln\left(\frac{e^{-\theta/T}}{1-e^{-\theta/T}}\right) + \ln\left[\left(\frac{2\pi mk}{h^2}\right)^{3/2}k\right]$$

10.4

$$C_v = 3R^\circ\left[4D\left(\frac{\theta_D}{T}\right) - \frac{3\theta_D/T}{\exp(\theta_D/T)-1}\right] \quad \text{Eq. (10.20)}$$

$$D\left(\frac{\theta_D}{T}\right) = 3\left(\frac{T}{\theta_D}\right)^3\int_0^{\theta_D/T}\frac{u^3}{e^u-1}\,du \quad \text{Eq. (10.21)}$$

$$\lim_{T\to 0} D\left(\frac{\theta_D}{T}\right) = \lim_{T\to 0} 3\left(\frac{T}{\theta_D}\right)^3\int_0^\infty \frac{u^3}{e^u-1}\,du$$

(see Appendix E)

$$= \lim_{T\to 0}\left(\frac{3\pi^4}{15}\right)\left(\frac{T}{\theta_D}\right)^3$$

$$\lim_{T\to 0}\frac{3\theta_D/T}{e^{\theta_D/T}-1} = \lim_{T\to 0} 3\left(\frac{\theta_D}{T}\right)e^{-\theta_D/T} = 0$$

$$C_v = 3Nk\,\frac{4\pi^4}{5}\left(\frac{T}{\theta_D}\right)^3 \quad \text{Eq. (10.22)}$$

10.5 $F = -kT\ln Q(T,V,N)$ Eq. (8.26b)

Eq. (10.10) applies equally well to 2-dim. case:

$$\ln Q = -\frac{N\phi(0,V/N)}{2kT} + \int_0^\infty\left[\frac{h\nu}{2kT} - \ln\left(e^{h\nu/kT}-1\right)\right]g\left(\nu,\frac{V}{N}\right)d\nu$$

But $g(\nu,\frac{V}{N})$ will be given by, according to Debye's model,

$$g(\nu, V/N) = \frac{4\pi A\nu^2}{c^2} \qquad \nu_m = \frac{Nc^2}{\pi A} \qquad \text{(Example 10.1)}$$

Thus

$$F(T,V,N) = \frac{N\phi(0,\frac{V}{N})}{2} - kT\int_0^{\nu_m}\left[\frac{h\nu}{2kT} - \ln\left(e^{h\nu/kT}-1\right)\right]\left(\frac{4\pi A\nu^2}{c^2}\right)d\nu$$

10.6 $$\frac{\sigma_U}{\bar{U}} = \frac{T\sqrt{k C_v}}{\bar{U}}$$

$T \to \infty \qquad C_v = 3Nk \qquad \dfrac{\sigma_U}{\bar{U}} = \dfrac{kT\sqrt{3N}}{\bar{U}}$

$T \to 0, \qquad C_v = \dfrac{12\pi^4}{5} Nk\left(\dfrac{T}{\theta_D}\right)^3 \qquad \dfrac{\sigma_U}{\bar{U}} = \dfrac{kT}{\bar{U}}\sqrt{\dfrac{36}{5}\pi^4\left(\dfrac{T}{\theta_D}\right)^3}$

10.7 See Example 1.2 for radiation pressure and C_v

$p_r = \dfrac{n^2 4\sigma}{3c_\ell} T^4 \qquad (C_v)_r = \dfrac{n^2 16\sigma}{c_\ell} T^3 V$

$p_D = -\dfrac{\partial U_0}{\partial V} + \dfrac{\gamma U_D}{V} \qquad$ Eq. (10.31)

$(C_v)_D = 9Nk\left(\dfrac{T}{\theta_D}\right)^3 \displaystyle\int_0^{\theta_D/T} \dfrac{u^4 e^u}{(e^u - 1)^2}\, du \qquad$ Eq. (10.20)

$p = p_D + p_r \quad , \quad C_v = (C_v)_D + (C_v)_r$

At 300°K, $\quad (C_v)_D \approx \underline{6 \dfrac{\text{cal}}{\text{g-mole } ^\circ\text{C}}}$ (for monatomic solids)

$(C_v)_r \approx \dfrac{(1.5)^2 16\,(5.67\times10^{-5})}{3\times10^{10}}(300)^3(10)\times 0.239\times10^{-7}$

$= \underline{\underline{4.4\times10^{-13}\ \text{cal/gmole}\ ^\circ\text{C}}}$ (for $n \approx 1.5$, $V \approx 0.01 \dfrac{\text{liter}}{\text{g-mole}}$)

$U_D \sim (C_v)_D T = 6\times300 = 1800$ cal/g-mole

$p_D \sim \dfrac{\gamma U_D}{V} \approx \dfrac{2\cdot1800}{10} = 360 \dfrac{\text{cal}}{\text{cm}^3} = \underline{\underline{1.5\times10^{10} \dfrac{\text{dynes}}{\text{cm}^2}}}$

$p_r = \dfrac{n^2 4\sigma T^4}{3c_\ell} \approx 10^{-12}\dfrac{\text{cal}}{\text{cm}^3} \approx \underline{\underline{4\times10^{-5}\dfrac{\text{dynes}}{\text{cm}^2}}}$

10.8 From Eq. (10.36): $\quad \bar{\xi} - \xi_e = \dfrac{\int_{-\infty}^{\infty} x\, e^{-\phi(x)/kT}\, dx}{\int_{-\infty}^{\infty} e^{-\phi(x)/kT}\, dx} \qquad x = (\xi - \xi_e)$

From Eq. (10.35) $\quad \phi(x) = \dfrac{1}{2}\left(\dfrac{d^2\phi}{dx^2}\right)_{x=0} x^2 + \dfrac{1}{6}\left(\dfrac{d^3\phi}{dx^3}\right)_{x=0} x^3 + \cdots = ax^2 + bx^3 + \cdots$

$$\bar{\xi} - \xi_e = \frac{\int_{-\infty}^{\infty} e^{-ax^2/kT}\left[x\left(1 - bx^3/kT + \cdots\right)\right] dx}{\int_{-\infty}^{\infty} e^{-ax^2/kT}\left[1 - bx^3/kT + \cdots\right] dx} = -\frac{3kT\, b}{4a^2} \qquad \text{Eq. (10.37)}$$

10.9 Fundamental equation: $F = -NkT \ln\left(\frac{v_f\, e}{\Lambda^3}\right) + \frac{N\phi}{2}$, Eq. (10.42)

$$\mu = \left(\frac{\partial T}{\partial p}\right)_h = \frac{1}{c_p}\left[T\left(\frac{\partial v}{\partial T}\right)_p - v\right] \qquad \text{(Example 9.3)}$$

$$c_p - c_v = \frac{T v \beta^2}{\kappa_T} \qquad \text{(general material relation, see any classical thermo. text)}$$

$$c_v = T\left(\frac{\partial s}{\partial T}\right)_V = -T\left(\frac{\partial^2 F}{\partial T^2}\right)_V$$

$$\kappa_T = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T = -\frac{1}{V}\frac{1}{\left(\frac{\partial p}{\partial V}\right)_T} = \frac{1}{V}\frac{1}{\left(\frac{\partial^2 F}{\partial V^2}\right)_T}$$

$$\beta = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p = \frac{1}{V}\left[-\frac{\left(\frac{\partial p}{\partial T}\right)_V}{\left(\frac{\partial p}{\partial V}\right)_T}\right] = -\frac{1}{V}\frac{\left(\frac{\partial^2 F}{\partial T \partial V}\right)}{\left(\frac{\partial^2 F}{\partial V^2}\right)_T}$$

10.10 Speed of sound $= a \equiv \sqrt{\left(\frac{\partial p}{\partial \rho}\right)_s} = \sqrt{-v^2\left(\frac{\partial p}{\partial v}\right)_s}$

$$\left(\frac{\partial p}{\partial v}\right)_s = \left(\frac{\partial p}{\partial T}\right)_s\left(\frac{\partial T}{\partial v}\right)_s = \frac{\left(\frac{\partial s}{\partial T}\right)_p}{\left(\frac{\partial s}{\partial p}\right)_T}\frac{\left(\frac{\partial s}{\partial v}\right)_T}{\left(\frac{\partial s}{\partial T}\right)_v} = \frac{\frac{c_p}{T}}{\left(\frac{\partial v}{\partial p}\right)_T \frac{c_v}{T}}$$

$$= \frac{-c_p}{v \kappa_T c_v}$$

c_p, c_v, κ_T all given in solution of Prob. 10.9

10.11 See Solution of Prob. 10.9 for β.

10.12 For a two-dimensional monatomic ideal gas: (Prob. 3.4)

$$Z = \sum_i g_i e^{-\epsilon_i/kT} = \frac{1}{h^2}\iint_A \iint_{-\infty}^{\infty} \exp\left(-\frac{p_u^2 + p_v^2}{2mkT}\right) dp_u\, dp_v\, dx\, dy = \frac{A}{h^2}(2\pi mkT) \equiv \frac{A}{\lambda^2}$$

$$F = -kT \ln Q = -kT \ln\left(\frac{A^N}{N!\,\lambda^{2N}}\right) = -NkT \ln\left(\frac{Ae}{\lambda^2}\right) \qquad \text{compare with Eq. (10.40)}$$

For a cell-model liquid: $F(T, A, N) = -NkT \ln\left[\frac{A_f(T,A)\, e}{\lambda^2}\right] + \frac{N\phi(0,A)}{2}$

(compare with Eq. (10.42))

10.13 From Eqs. (10.42) and (10.43):

$$F = -NkT \ln\left[\frac{(v-b)\, e}{\Lambda^3}\right] - \frac{Na}{v}, \qquad C_v = -T\left(\frac{\partial^2 F}{\partial T^2}\right)_{V,N} = \frac{3}{2}Nk$$

The result is the same as that of a monatomic ideal gas because (1) in the formulation internal modes of motion in the molecule are neglected and (2) the VDW gas is a hard-sphere-with-weak-attraction gas.

CHAPTER 11

11.1 We must average the vertical travel, $l\cos\phi$, over the projected solid angle, $(r^2\sin\phi\, d\theta d\phi)\cos\phi$, so

$$l_{vert} = \frac{\int_0^{\pi/2}(l\cos\phi)\sin\phi\cos\phi\, d\phi}{\int_0^{\pi/2}\sin\phi\cos\phi\, d\phi} = \frac{1/3}{1/2}\, l = \underline{\frac{2}{3}\, l}$$

11.2 If the lengths vary uniformly, $F(\xi) = \text{Const.}$ such that

$$1 = \int_0^{l_0} \text{Const}\, d\xi = \text{Const}\times l_0 \qquad \text{or} \qquad F(\xi) = 1/l_0$$

Thus
$$\bar{l} = \int_0^{l_0} \xi F(\xi)\, d\xi = \frac{1}{l_0}\cdot\frac{l_0^2}{2} = \underline{\frac{l_0}{2}} \qquad \text{(no suprise)}$$

Now the distribution of those straws touching the line will be increased in direct proportion to the length of the straw, since the longer the straw is, the more likely it will be to reach the line. Thus

$$F_{touching}(\xi) \sim \xi F(\xi) \quad \text{so} \quad l_{touching} = \frac{\int_0^{l_0}\xi(\xi/l_0)\, d\xi}{\int_0^{l_0}(\xi/\xi_0)\, d\xi}$$

or
$$l_{touching} = \frac{\frac{1}{3}l_0^3}{\frac{1}{2}l_0^2} = \frac{2}{3}l_0 \quad \text{and} \quad \frac{l_{touch}}{l_{touching}} = \frac{2}{3}\frac{2}{1} = \underline{\frac{4}{3}}$$

11.3 $\xi_{most\ probable}$ = value that maximizes $F(\xi)$. This value is $\xi = 0$.

$$\overline{\xi^2} = \int_0^\infty \xi^2 F(\xi)\, d\xi = \int_0^\infty \xi^2 \frac{\exp(-\xi/l)}{l}\, d\xi = 2l^2, \quad \underline{\xi_{rms} = \sqrt{2}\, l}$$

$$\frac{0.0001}{l_{air}} = 0.0001\,\frac{\sqrt{2}\pi n\sigma^2}{1.051} = \frac{\frac{p}{kT}\sigma^2}{2370} = \frac{1}{2370}\,\frac{1.013\times10^6\,(3.7\times10^{-8})^2}{1.38\times10^{-16}(298)} = \underline{14.2}$$

Fraction with $\xi > 14.2 = 1-(1-e^{-14.2}) = \underline{7\times10^{-7}}$. This is a very small fraction but $1\,cm^3$ contains 2.5×10^{19} molecules, or 1.75×10^{13} with $\xi > 0.001$!

11.4 From previous problem $\ell = \frac{.0001}{14.2} = \underline{0.00000704\ \text{cm}}$ and at standard conditions, $\ell_0 = n^{-1/3} = \sqrt[3]{kT/p} = \sqrt{1.38\times10^{-16}(298)/1.013\times10^{6}}$ $= \underline{3.43\times10^{-7}\text{cm}}$ or $1/20.5$ of ℓ.

At 200 mi. elevation, we find from Mark's Mech. Engr. handbook (or other comparable sources) that the density is reduced by a factor of 1.1×10^{20}. ℓ and ℓ_0 will be increased by this factor so:

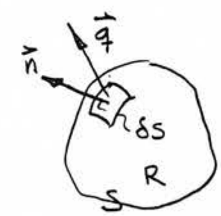
$$\ell = 7.8\times10^{20-6}\ \text{cm} = \underline{7.8\times10^{9}\ \text{km}}\ ; \quad \ell_0 = \underline{3.8\times10^{8}\ \text{km}}$$

A "macroscopic" volume should include many mean free paths. Thus

$$\text{Vol}_{macro} = \mathcal{O}(10\ell)^3 = \mathcal{O}(10^{-15}\text{cm}) \text{ at sea level}$$
$$= \mathcal{O}(10^{32}\text{km}) \text{ at 200 mi. elev.}$$

A macroscopic volume is on the order of the dimensions of the solar system at 200 mi. elev.. Thus no continuum computations are possible at this height.

11.5 Consider a control volume. The first law says:



$$-\int_S \vec{q}\cdot(\vec{n}\,ds) = \int_R \frac{\partial u}{\partial t}\,dR$$

but $q = -k\vec{\nabla}T$ and Gauss' Theorem is $\int_S \vec{A}\cdot(\vec{n}\,ds) \equiv \int_R \vec{\nabla}\cdot\vec{A}\,dR$

so: $$-\int_R\left(-\vec{\nabla}\cdot k\vec{\nabla}T + \frac{\partial u}{\partial t}\right)dR = 0$$

finally if we write $u = \rho c(T - T_{ref})$ & take ρ, c and k as constants: $$\int_R\left(k\nabla^2T - \rho c\frac{\partial T}{\partial t}\right)dR = 0$$

but the integrand must vanish identically since dR is arbitrary, and $k/\rho c = \alpha$, so

$$\underline{\underline{\nabla^2 T = \frac{1}{\alpha}\frac{\partial T}{\partial t}}}$$

11.6 $\left.\begin{array}{l}\lambda \sim \rho \bar{c} \ell \sim T^{1/2} \\ \mu \sim \rho \bar{c} \ell \sim T^{1/2}\end{array}\right\}$ ℓ and μ are independant of p

$D \sim \bar{c} \ell \sim T^{1/2}/n \sim T^{3/2}/p \, \Big\}$ $D \sim p^{-1}$

11.7 From the solution of Prob. 2.19 we have for a 2-dimensional gas $\quad J_{molecules} = \frac{n\bar{c}}{\pi}$ and $\bar{c} = \sqrt{\frac{\pi k T}{2m}}$

Thus: $\quad J^{\pm}_{mom} = \frac{n\bar{c}}{\pi} m \left(u_r \pm \alpha \ell \left.\frac{\partial u}{\partial y}\right|_{y_r}\right)$ so

$$J_{mom} = -\mu \frac{\partial u}{\partial y} = J^{-}_{mom} - J^{+}_{mom} = -\frac{2\bar{c}}{\pi} \rho \alpha \ell \frac{\partial u}{\partial y}$$

Now $\ell = \frac{1}{n(2\sigma)}$ for a 2-dim gas so

$$\underline{\mu = \frac{2\alpha}{\pi} \rho \bar{c} \ell = \frac{\alpha}{\sigma} \sqrt{\frac{mkT}{2\pi}}}$$

11.8 The derivation in this case is perfectly analogous to that in 11.5. The result is:

$$\nabla^2 n = \frac{1}{D} \frac{\partial n}{\partial t}$$

where $D = D \frac{ft^2}{sec}$ or $\frac{cm^2}{sec}$ and $n = n \frac{lbm}{ft^3}$ or $\frac{gm}{cm^3}$, for example.

11.9 We shall illustrate this problem using data for one case, namely steam

T	p	λ	c_p	c_v	γ	ρ	μ	$Pr = \frac{\mu c_p}{\lambda}$	$\frac{9}{4}\left(\gamma - \frac{5}{9}\right)\frac{1}{\gamma}$
100°C	atm	$.543 \times 10^{-4}$	8.14	6.15	1.325	.000596	.000130	0.96	1.31
		$\frac{cal}{cm\ sec\ °C}$	$\frac{cal}{gmole\ °C}$			gm/cm³	gm/cm sec	They differ by 36%.	

The quantities $\frac{\lambda}{\mu c_v}$ & $4\gamma/(9\gamma-5)$ will also differ by the same percentage. The difference arises because $(\beta/\alpha)_{tr} < 5/2$ for steam & because steam is not really an ideal gas.

11.10 $\lambda = \lambda_t + \lambda_i = \left[\left(\frac{\beta}{\alpha}\right)_t c_{v_t} + \left(\frac{\beta}{\alpha}\right)_i c_{v_i} \right] \mu$

but $\left(\frac{\beta}{\alpha}\right)_t c_{v_t} = \left(\frac{\beta}{\alpha}\right)_t \left[\frac{2}{2}(\gamma - 1) c_v \right]$ since $c_p - c_v = R^\circ$

and $\left(\frac{\beta}{\alpha}\right)_i c_{v_i} = 1\left[1 - \left(\frac{2}{2}\gamma - 1\right)\right]$

Thus $\underline{\lambda = \left[\left(\frac{\beta}{\alpha}\right)_t (\gamma - 1) + (2 - \gamma) \right] \mu c_v}$

& $\underline{P_r = c_p \mu / \lambda = \gamma / \left[\left(\frac{\beta}{\alpha}\right)_t (\gamma - 1) + (2 - \gamma) \right]}$

11.11 $\mu = \frac{1}{2} \alpha \rho \bar{c} \, l \simeq \frac{1}{2}(1.14)(mn)\sqrt{\frac{8kT}{\pi m}} \frac{1.051}{\sqrt{2} n \pi \sigma^2} = 0.215 \frac{\sqrt{kmT}}{\sigma^2}$

$= \frac{.215}{(4.6)^2 10^{-16}} \sqrt{1.38 \frac{18.02}{6.03} 5 \times 10^{-16-23+2}} = 1.464 \times 10^{-4} \frac{gm}{cm\ sec}$

$= \underline{0.01464 \text{ centipoise}}$

where have used the rough sphere value of $\alpha = 1.14$. The resulting value of μ is still below the experimental value of 0.017 centipoise

$\lambda = \mu c_v \left[\frac{1}{4}(9\gamma - 5) \right] = 1.464 \times 10^{-4} \left(3 \frac{R^\circ}{M}\right) \left[\frac{1}{4}\left(9 \times \frac{4}{3} - 5\right) \right]$

$= .848 \times 10^{-4} \frac{gm}{cm\ sec} \cdot \frac{cal}{gm - {}^\circ K} = \underline{0.0211 \text{ Btu/hr ft}^\circ R}$

which compares nicely with the experimental value of $\lambda = 0.021$ Btu/hr ft°R.

Finally $P_r = \frac{4\gamma}{9\gamma - 5} = \frac{16}{3}\frac{1}{7} = \underline{0.762}$. The fact that this is below the experimental value of 0.94 reflects the fact that the simple theory under-predicts μ.

11.12 $\mu = \frac{\alpha}{2}\left(\rho_{H_2O} \bar{c}_{H_2O} l_{H_2O} + \rho_{CO_2} c_{CO_2} l_{CO_2}\right)$ where $\alpha \simeq 1.14$

$\rho_{H_2O} = 0.4 \frac{p}{RT} = 0.88 \times 10^{-3} gm/cm^3$; $\rho_{CO_2} = 3.22 \times 10^{-3} gm/cm^3$

$\bar{c}_{H_2O} = \sqrt{\frac{8kT}{\pi m}} = 1.085 \times 10^5 cm/sec$; $\bar{c}_{CO_2} = .694 \times 10^5 cm/sec$

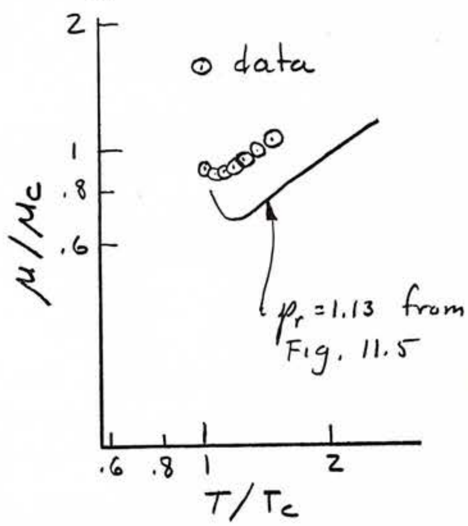
11.12, cont'd. $\quad \lambda_{H_2O} = \frac{1.051}{\sqrt{2}\pi n \sigma^2} = 1.525 \times 10^{-5}\,cm \; ; \quad \ell_{CO_2} = 1.525 \times 10^{-5}\,cm$

put all these in the expression for μ and get:

$$\mu = 2.76 \times 10^{-4} \frac{gm\text{-}sec}{cm} = \underline{2.76 \times 10^{-4}\ poise}$$

11.13 From the latest steam tables we get $\mu_{crit} = 359\,\mu poise$ by interpolation. Then

$T°R$	$\frac{T}{T_c}$	μ	$\frac{\mu}{\mu_c}$
$p = 250\,atm,\ p_r = 1.13$			
1752	1.5	389	1.08
1662	1.43	371	1.03
1572	1.35	353	.98
1482	1.27	336	.94
1392	1.20	321	.90
1302	1.12	310	.86
1212	1.04	321	.90



The comparison is not very good in the case of steam near the critical point. The prediction is low by about 30% in this range.

11.14 We have $\frac{1}{\sigma} \sim T^5 \int_0^{\Theta/T} \frac{x^5\,dx}{(e^x-1)(1-e^{-x})}$, so for $\frac{\Theta}{T} \Rightarrow \infty$ the integral $\Rightarrow$ constant and $\underline{\sigma \sim T^{-5}}$ (11.70)

For $\frac{\Theta}{T} \Rightarrow 0$, $\frac{1}{\sigma} \sim T^5 \int_0^{\Theta/T} \frac{x^5\,dx}{(x)(x)} \sim T^5 \left(\frac{\Theta}{T}\right)^4$ so

$$\underline{\sigma \sim T^{-1}} \quad (11.71)$$

CHAPTER 12

12.1 Eq. 12.7 can be written immediately since the pair does not lose momentum in the collision. Rearranging it we obtain

$$m_i \vec{c}_i = m_0 \vec{G} - m_j (\underbrace{\vec{c}_j}_{\equiv \vec{c}_i - \vec{g}_{ij}})$$

so: $\quad m_0 \vec{c}_i = m_0 \vec{G} + m_j \vec{g}_{ij} \quad$ or $\quad \underline{\vec{c}_i = \vec{G} + M_j \vec{g}_{ij}}$

The remaining equations in Eq. (12.8) can be written down (following this result) immediately, by symmetry.

Next we write the energy equation for the collision

$$m_i \vec{c}_i^{\,2} + m_j \vec{c}_j^{\,2} = m_i \vec{c}_i^{\,\prime 2} + m_j \vec{c}_j^{\,\prime 2}$$

and substitute equations 12.8 for $\vec{c}_i, \vec{c}_j, \vec{c}_i', \vec{c}_j'$.

The result, after simplification, is

$$m_0 G^2 + \frac{m_i m_j}{m_0} g^2 = m_0 G^2 + \frac{m_i m_j}{m_0} g'^2 \quad \text{or:} \quad \underline{g = g'}$$

12.2 multiply Eq. (12.11a) by $(\vec{r}_i - \vec{r}_j)$ in a cross product. Then since $\vec{r}_i - \vec{r}_j$ & $\vec{F}$ are colinear the right-hand product vanishes and $(\vec{r}_i - \vec{r}_j) \times \frac{d}{dt}(\vec{c}_i - \vec{c}_j) = 0$

but

$$(\vec{r}_i - \vec{r}_j) \times \frac{d}{dt}(\vec{c}_i - \vec{c}_j) = \frac{d}{dt}\left[(\vec{r}_i - \vec{r}_j) \times (\vec{c}_i - \vec{c}_j)\right] - \underbrace{(\vec{c}_i - \vec{c}_j) \times (\vec{c}_i - \vec{c}_j)}_{= 0}$$

$\therefore \quad \frac{d}{dt}\left[(\vec{r}_i - \vec{r}_j) \times (\vec{c}_i - \vec{c}_j)\right] = 0 \quad$ or

$$\underline{(\vec{r}_i - \vec{r}_j) \times (\vec{c}_i - \vec{c}_j) = \vec{K}}, \text{ a const vector}$$

12.3 To simplify the required integration, note that:

$$m_1\vec{C}_1^{\,2} + m_2\vec{C}_2^{\,2} = (m_1+m_2)\vec{G}^{\,2} + \frac{m_1 m_2}{m_1+m_2}\vec{g}^{\,2}$$

so

$$N_{12} = \iint_{C_1\,C_2} n_1\left(\frac{m_1}{2\pi kT}\right)^{3/2} n_2\left(\frac{m_2}{2\pi kT}\right)^{3/2} \exp\left\{-\left(m_1\vec{C}_1^{\,2}+m_2\vec{C}_2^{\,2}\right)/2kT\right\}$$

$$\cdot\, g\,\sigma_{12}^2(4\pi C_1^2 dC_1)(4\pi C_2^2 dC_2)\underbrace{\int_0^{\pi/2}\cos\psi\sin\psi\,d\psi}_{1/2}\ \underbrace{\int_0^{2\pi} d\epsilon}_{2\pi}$$

can be transformed into

$$N_{12} = 2\pi\sigma_{12}^2 n_1 n_2 \frac{(m_1 m_2)^{3/2}}{(kT)^3}\iint_{G\,g} G^2 g^3 \exp\left\{-\frac{1}{2kT}\left[(m_1+m_2)G^2 + \frac{m_1 m_2}{m_1+m_2}g^2\right]\right\} \cdot dG\,dg$$

The integration yields

$$\underline{N_{12} = 2n_1 n_2\sigma_{12}^2\sqrt{\frac{2\pi kT(m_1+m_2)}{m_1 m_2}}}$$

12.4 $n = \int \alpha \exp\left[-\frac{m\beta}{2}\left(\vec{c}-\frac{\vec{b}}{\beta}\right)^2\right] d\vec{c}$; let $\vec{c}-\frac{\vec{b}}{\beta} \equiv \vec{A}$

$$n = \alpha\int \exp\left[-\frac{m\beta}{2}\vec{A}^{\,2}\right] d\vec{A} = \alpha\left[\frac{\sqrt{\pi}}{\sqrt{\frac{m\beta}{2}}}\right]^3 ; \quad \underline{\alpha = n\left(\frac{m\beta}{2\pi}\right)^{3/2}}$$

$$\rho\vec{c}_0 = \int m\vec{c}\,f\,d\vec{c} = m\int\left(\frac{\vec{b}}{\beta}+\left[\vec{c}-\frac{\vec{b}}{\beta}\right]\right)f\,d\left(\vec{c}-\frac{\vec{b}}{\beta}\right)$$

$$= m\frac{\vec{b}}{\beta}n + \underbrace{\text{integral of an odd function}}_{=0} ; \quad \underline{\vec{b} = \vec{c}_0\beta}$$

so

$$\frac{3}{2}kT = \frac{m}{2n}\underbrace{\int \mathbb{C}^2 f(\vec{\mathbb{C}})\,d\vec{\mathbb{C}}}_{\alpha\,\pi^{3/2}/\left(\frac{m\beta}{2}\right)^{5/2}}$$

where $\vec{\mathbb{C}} \equiv \vec{c}-\vec{c}_0$, the thermal velocity, and $d\vec{c} = d\vec{\mathbb{C}}$

but $\alpha = n\left(\frac{m\beta}{2\pi}\right)^{3/2}$ so $\underline{\beta = \frac{1}{kT}}$

12.5 Enter Eq. 12.28 with $\Phi_i = \Phi_i' = m_i = \text{constant}$ and get

$$\iiiint \Phi_i (f_i' f_j' - f_i f_j)\, g\, b\, db\, d\epsilon\, d\Omega_i\, d\Omega_j = 0$$

Thus if we multiply Eq. 12.16 by $d\Omega_i$ & integrate over $d\Omega_i$ without also summing over i, we get

$$\int_{\Omega_i} m_i \left(\frac{\partial f_i}{\partial t} + \vec{c}_i \frac{\partial f_i}{\partial \vec{r}} + \vec{F}_i \frac{\partial f_i}{\partial \vec{c}_i} \right) d\Omega_i = 0$$

This is only true if the term in parentheses vanishes. Thus we can drop the $\sum_i$ from Eq. 12.53 and Eq. 12.59 follows

12.6 We expand the species continuity equation as follows

$$\frac{\partial \rho_i}{\partial t} + \vec{\nabla}\cdot\rho_i\vec{c}_i = \frac{\partial \rho_i}{\partial t} + \underbrace{\vec{\nabla}\cdot\rho_i\vec{c}_0}_{\vec{c}_0\cdot\nabla\rho_i + \rho_i\vec{\nabla}\cdot\vec{c}_0} + \underbrace{\vec{\nabla}\cdot\rho_i\vec{\mathbb{C}}_i}_{\equiv \vec{\nabla}\cdot\vec{J}_{m_i}}$$

$$\therefore \quad \underline{\frac{D\rho_i}{Dt} + \rho_i\vec{\nabla}\cdot\vec{c}_0 + \vec{\nabla}\cdot\vec{J}_{m_i} = 0}$$

12.7

$$\underbrace{\rho\left[\frac{DE}{Dt} + \frac{1}{\rho}\frac{Dp}{Dt}\right]}_{\rho\frac{Dh}{Dt} + \frac{p}{\rho}\frac{D\rho}{Dt}} = \underbrace{-\vec{\nabla}\cdot J_\epsilon}_{=\lambda\nabla^2 T} - \underbrace{p_{k\ell} : \vec{\nabla}\vec{C}_0 + \sum \vec{F}_i\cdot\vec{J}_{m_i}}_{=0} + \frac{Dp}{Dt}$$

where the differential enthalpy is $dh = c_p\, dT + \frac{1}{\rho}\Big[1 - \underbrace{\frac{1}{v}\frac{\partial v}{\partial T}\Big|_p T}_{=0}\Big]dp$

so

$$\rho c_p \frac{DT}{Dt} + \cancel{\frac{Dp}{Dt}} + \frac{p}{\rho}\underbrace{\frac{D\rho}{Dt}}_{=0} = \lambda\nabla^2 T + \cancel{\frac{Dp}{Dt}}$$

$$\underline{\frac{1}{\alpha}\frac{DT}{Dt} = \lambda\nabla^2 T}$$

12.8 The steady Boltzmann equation becomes

$$0+\vec{c}\cdot\frac{\partial f}{\partial \vec{r}}+\vec{F}\cdot\frac{\partial f}{\partial \vec{c}}=0 \qquad \text{or} \qquad \vec{c}\cdot\frac{\partial \ln f}{\partial \vec{r}}=-\vec{F}\cdot\frac{\partial \ln f}{\partial \vec{c}}$$

but f has to take the form

$$f=n(\vec{r})\left(\frac{m}{2\pi kT}\right)^{3/2}\exp\left(-\frac{m\vec{c}^{\,2}}{2kT}\right)$$

put this in the Boltzmann equation and get:

$$\vec{c}\cdot\frac{\partial \ln n}{\partial \vec{r}}=-\vec{F}\cdot\left[-\frac{m\vec{c}}{kT}\right] \qquad \text{or} \qquad n(r)=C_1\exp\left[+\int\frac{m\vec{F}}{kT}d\vec{r}\right]$$

but $n(\vec{F}=0)=n_o$ so $C_1=n_o$ and $\vec{F}=-\frac{dU}{d\vec{r}}$ so

$$n(r)=n_o\exp\left[-\frac{mU}{kT}\right]$$

Thus:

$$\underline{f=n_o\left(\frac{m}{2\pi kT}\right)^{3/2}\exp\left[-\frac{m}{kT}\left(\frac{\vec{c}^{\,2}}{2}+U(\vec{r})\right)\right]}$$

12.9 a.) For earth's gravity, $U=gz+\text{Const.}$; $\vec{F}=-\vec{g}$
$=-g\vec{i}$

so $\underline{f(z,\vec{c})=n_o\left(\frac{m}{2\pi kT}\right)^{3/2}\exp\left(-\frac{m}{kT}\left[\frac{\vec{c}^{\,2}}{2}+gz\right]\right)}$

where n_o = density at $g=0$, so const. $=0$.

b.) $U=\int-\vec{F}\,d\vec{r}=-\int\omega^2 r\,dr=-\frac{\omega^2r^2}{2}+\text{const}$

but $U=0$ where $r=0$ & $\omega r\equiv C_t$ so $\underline{U=-\frac{C_t^2}{2}}$

Then

$$\underline{f(C_t,\vec{c})=n_o\left(\frac{m}{2\pi kT}\right)^{3/2}\exp\left(-\frac{m}{2kT}\left[C_t^2+\vec{c}^{\,2}\right]\right)}$$

12.10 We begin with Eq. (12.78) $\underbrace{-\frac{\partial f_i}{\partial t}}_{=0 \text{ since steady}} + \vec{c}_i \cdot \frac{\partial f_i}{\partial \vec{r}} + \underbrace{\vec{F}_i}_{=0} \cdot \frac{\partial f_i}{\partial \vec{c}_i} = \frac{f_i - \bar{f}_i^{(0)}}{\tau}$

so $\vec{c}_i \frac{\partial f_i}{\partial \vec{r}} = u\frac{\partial f_i}{\partial x} + v\frac{\partial f_i}{\partial y} + w\frac{\partial f_i}{\partial t} = 0 + v\frac{\partial f_i}{\partial y} = 0$

and Eq. (12.79) follows. The steps leading to Eq. (12.82) are obvious. Finally we must integrate:

$$\mu = -\frac{m\ell}{\bar{c}}\iiint U V^2 \frac{\partial f^0}{\partial U}\, dU\,dV\,dW = -\frac{m\ell}{\bar{c}}\iint V^2 dV dW \underbrace{\int U\frac{\partial f^{(0)}}{\partial U}\,dU}_{f^{(0)}U\Big]_{-\infty}^{\infty} - \int_{-\infty}^{\infty} f^0\, dU}$$

$$\mu = +\frac{m\ell}{\bar{c}}\iiint_{-\infty}^{\infty} V^2 f^{(0)}\, dU\,dV\,dW = \underline{\frac{m\ell}{\bar{c}}\, n\overline{V^2}}$$

12.11 Put $f_i = f_i^{(0)} + \epsilon f_i^{(1)} + \epsilon^2 f_i^{(2)} + \cdots$ in $\epsilon\left(\frac{\partial f}{\partial t}\right)_{coll.} = \sum_j J(f_i f_j)$

so:

$$\epsilon\left(\frac{\partial f_i^{(0)}}{\partial t} + \vec{c}_i \cdot \frac{\partial f_i^{(0)}}{\partial \vec{r}} + \vec{F}_i \frac{\partial f_i^{(0)}}{\partial \vec{c}_i}\right) + \epsilon^2\left(\frac{\partial f_i^{(1)}}{\partial t} + \cdots\right) + \epsilon^3\left(\frac{\partial f^{(2)}}{\partial t} + \cdots\right)$$

$$= \sum_j \iiint \Big(f_i^{(0)'} f_j^{(0)'} + \epsilon\left[f_i^{(0)'} f_j^{(1)'} + f_j^{(0)'} f_i^{(1)'}\right] + \epsilon^2\left[f_i^{(0)'} f_j^{(2)'} + f_j^{(0)'} f_i^{(2)'} + f_i^{(1)'} f_j^{(1)'}\right] - \text{same w/o primes}\Big)\, g\, b\, db\, d\epsilon\, d\Omega;$$

collect all terms in like powers of ϵ:

ϵ^0 $$\underline{0 = \sum_j J(f_i^{(0)} f_j^{(0)})}$$

ϵ^1 $$\underline{\left(\frac{\partial f_i^{(0)}}{\partial t}\right)_{coll.} = \sum_j J(f_i^{(0)} f_j^{(1)}) + \sum_j J(f_j^{(0)} f_i^{(1)})}$$

ϵ^2 $$\underline{\left(\frac{\partial f_i^{(1)}}{\partial t}\right)_{coll.} = \sum_j\left(J(f_i^{(0)} f_j^{(2)}) + J(f_j^{(0)} f_i^{(2)}) + J(f_i^{(1)} f_j^{(1)})\right)}$$

The 3rd order equation follows the same pattern.

12.12 a) After a few collisions, the discontinuity of temperature will iron out and a continuous distribution, $f(\vec{c}, \vec{r}, t)$ will be obtained. Since $\lambda/L \ll 1$, the field can be represented by $f = f^{(0)} + f^{(1)}$, and the hydrodynamic equations (with b.c., $T = T_1$ on B) will be valid.

b) Since $\vec{c}_0 = 0$, continuity becomes $\frac{\partial \rho}{\partial t} = 0$, or $\rho \neq \rho(t)$.
And the momentum eq. becomes $\vec{\nabla} p/\rho = 0$.
Finally the energy eq. reduces to $\sigma \nabla^2 T = 0$.
Since $\vec{\nabla} p = 0$ there is no net force on the disk.

c) When $\lambda \gg L$ a temperature discontinuity can exist and the momentum of incoming and outgoing molecules will differ.

pressure on face A, $p_A = \frac{1}{3} nm\overline{c^2} = nkT$

pressure on face B, $p_B = \frac{1}{2} nkT + \frac{1}{2} nkT_1$

$$\Delta p\Big|_A^B = p_B - p_A = \frac{nk}{2}(T_1 - T) \; ; \; \text{net force} = \underline{\frac{nkA}{2}(T_1 - T)}$$

12.13 Assume: monatomic molecules, binary encounters, molecular chaos.

If we use subscript 1 to designate light molecules and 2 to designate heavy molecules, the Boltzmann equation for light molecules becomes:

$$\left(\frac{\partial f}{\partial t}\right)_{coll} = \iiint (f_1' f_2' - f_1 f_2)\, g_{12}\, b\,db\,d\epsilon\,d\Omega_2$$

where, because $M_2 \gg M_1$, $\vec{c}_{12}' \simeq \vec{c}_2$, $f_2'(\vec{c}_2') \simeq f_2(\vec{c}_2)$

$$\text{so} \quad \left(\frac{\partial f}{\partial t}\right)_{coll} = \iint (f_1' - f_1)\, g_{12}\, b\,db\,d\epsilon \int f_2\, d\Omega_2$$

$$\text{or} \quad \left(\frac{\partial f}{\partial t}\right)_{coll} = n_H \iint (f' - f_1)\, g_{12}\, b\,db\,d\epsilon$$

12.14 (a) $\vec{F}\cdot\frac{\partial f^{(0)}}{\partial\vec{c}} = -\frac{f^{(1)}}{\tau}$ $\qquad \vec{F} = \frac{e\vec{E}}{m}$

$$f^{(1)} = \frac{e\vec{E}\tau\cdot\vec{c}}{kT} f^{(0)} \qquad f = f^{(0)} + f^{(1)} = f^{(0)}\left(1 + \frac{e\vec{E}\tau\cdot\vec{c}}{kT}\right)$$

(b) $\bar{\vec{c}} = \frac{1}{n}\int \vec{c}\, f\, d\vec{c} = \left(\frac{m}{2\pi kT}\right)^{3/2}\left(\frac{\tau e\vec{E}}{kT}\right)\iiint_{-\infty}^{\infty} u^2 e^{-m(u^2+v^2+w^2)/2kT}\, du\, dv\, dw$

$$\bar{\vec{c}} = \frac{e\vec{E}\tau}{m}$$

Since $ne\bar{\vec{c}} = \sigma\vec{E}$ $\qquad \sigma = \left(\frac{ne^2\tau}{m}\right)$

12.15 Put $f_i = f_i^{(0)} + \epsilon f_i^{(1)}$ and $f_i' = f_i^{(0)} + \epsilon f_i^{(1)'}$

in Eq. (12.76) $\quad \left(\frac{\partial f_i}{\partial t'}\right) = \frac{1}{\epsilon}\sum_j J(f_i f_j)$

$$\frac{\partial f_i^{(0)}}{\partial t'} + \vec{c}_i\cdot\frac{\partial f_i^{(0)}}{\partial\vec{r}} + \vec{F}_i\cdot\frac{\partial f_i^{(0)}}{\partial\vec{c}_i} = \sum_j \iiint \left[f_i^{(0)'} f_j^{(1)'} + f_i^{(1)'} f_j^{(0)'} - f_i^{(0)} f_j^{(1)} - f_i^{(1)} f_j^{(0)}\right] g\, b\, db\, d\epsilon\, d\Omega_j$$

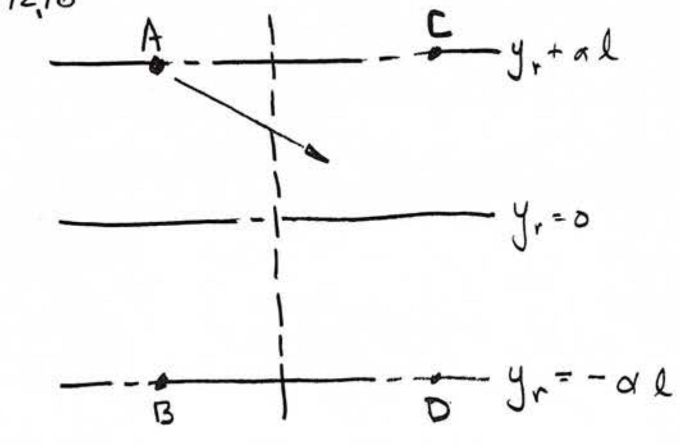
i.e. $\left(\frac{\partial f_i^{(0)}}{\partial t}\right)_{coll} = \sum_j J(f_i^{(0)} f_j^{(1)}) + \sum_j J(f_i^{(1)} f_i^{(1)})$ $\qquad$ Eq. (12.86)

$$f_i^{(1)} = f_i^{(0)}\phi_i, \quad f_i^{(1)'} = f_i^{(0)}\phi_i', \quad f_j^{(1)} \cdots\cdots$$

$$\left(\frac{\partial f_i^{(0)}}{\partial t}\right)_{coll.} = \sum_j \iiint f_i^{(0)} f_j^{(0)}\left(\epsilon\phi_i' + \epsilon\phi_j' - \epsilon\phi_i - \epsilon\phi_j\right) g\, b\, db\, d\epsilon\, d\Omega_j$$

Eq. (12.97a)

12.16



of the particles originating at A, some move across (¦) in the range:
$-\alpha l \le y \le \alpha l$
($\bar{c}$ at A $= \bar{c} + u_A$)

No. of particles from A down across (¦) $= \frac{n}{4}\bar{c} + \frac{1}{2} n u_A$ (since $\frac{1}{2}$ of particles go up)

" " " " C " " " $= \frac{n}{4}(\bar{c} - 2u_c)$

" " " " B up " " $= \frac{n}{4}(\bar{c} + 2u_B)$

" " " " D up " " $= \frac{n}{4}(\bar{c} - 2u_D)$

but $u_c = u_A$ and $u_B = u_D = (u_A - 2\alpha l \frac{\partial u}{\partial y})$

So the net flux of upward momentum across (¦) from left to right is:

$$J_m = \frac{n}{4}(\bar{c} + 2u_A)m\bar{v} - \frac{n}{4}(\bar{c} - 2u_A)m\bar{v} - \frac{n}{4}\left(\bar{c} + 2u_A - 4\alpha l \frac{\partial u}{\partial y}\right)m\bar{v} + \frac{n}{4}\left(\bar{c} - 2u_A + 4\alpha l \frac{\partial u}{\partial y}\right)m\bar{v}$$

$$J_m = 2n\alpha l m\bar{v}\frac{\partial u}{\partial y}$$

but by simple number conservation $n\bar{v} = \frac{n\bar{c}}{4}$

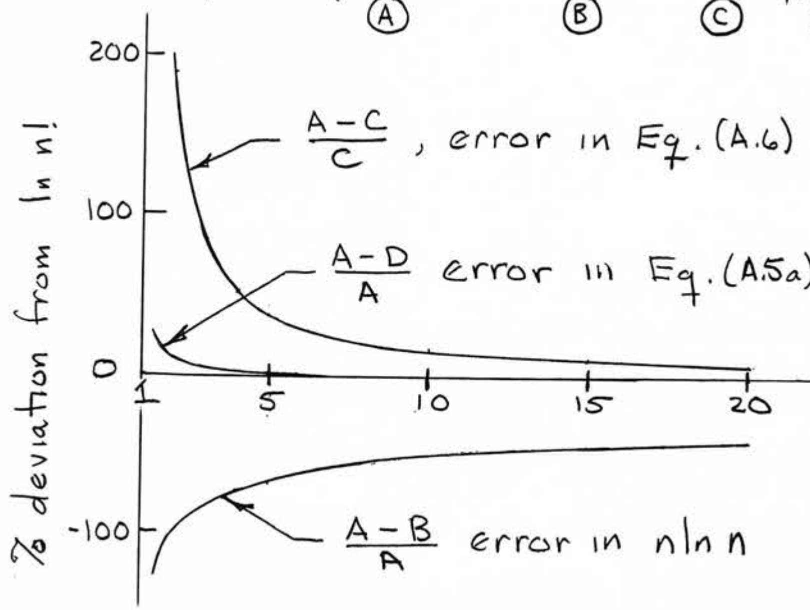
So $$J_m = \underbrace{\frac{1}{2}\rho\alpha l\bar{c}}_{\equiv \mu}\frac{\partial u}{\partial y}$$

this is the same as (J_m) horizontal.

APPENDICES A & B

A.1

n	$n!$	$\ln n!$	$\ln n$	$n \ln n$	$n\ln n - n$	$C + \frac{\ln 2\pi}{2} + \ln n/2$
1	1	0	0	0	−1	−.081
2	2	.693	.693	1.386	−.614	.752
3	6	1.79	1.099	3.297	.297	1.766
4	24	3.18	1.386	5.544	1.544	3.156
5	120	4.80	1.609	8.045	3.045	4.769
10	3.63×10^{6}	15.1	2.303	23.03	13.03	15.09
15	1.307×10^{12}	27.95	2.708	40.62	25.62	27.89
20	2.433×10^{18}	42.4	2.996	59.92	39.92	42.34
		A		B	C	D



We conclude that Eq (A.5a), while a little more complicated is extraordinarily accurate for small n. On the other hand, the approximation n ln n, while it converges to ln n! only at very large n, is a very simple approximation.

B.1 a) $\text{Area} = \pi(\frac{1}{2}D^2 + DL)$; $dA = (\pi D + \pi L)\,dD + (\pi D)\,dL = 0$

$V_o = \frac{\pi}{4}D^2 L$; $(\alpha\, 2\pi L D)\,dD + (\alpha \pi D^2)\,dL = 0$

so $\left.\begin{array}{r} \pi D + \pi L + \alpha\, 2\pi L D = 0 \\ \pi D + \alpha \pi D^2 = 0 \end{array}\right\}$ $\underline{\alpha = -\frac{1}{D}}$, $\underline{\underline{L = D}}$

B.1 Cont'd.)

b) $C = C_m(\frac{1}{2}\pi D^2 + \pi D L) + C_w(2\pi D + L)$

$$dC = (\pi C_m D + \pi C_m L + 2\pi C_w)dD + (\pi C_m D + C_w)dL = 0$$

$$(\alpha 2\pi L D)dD + (\alpha \pi D^2)dL = 0$$

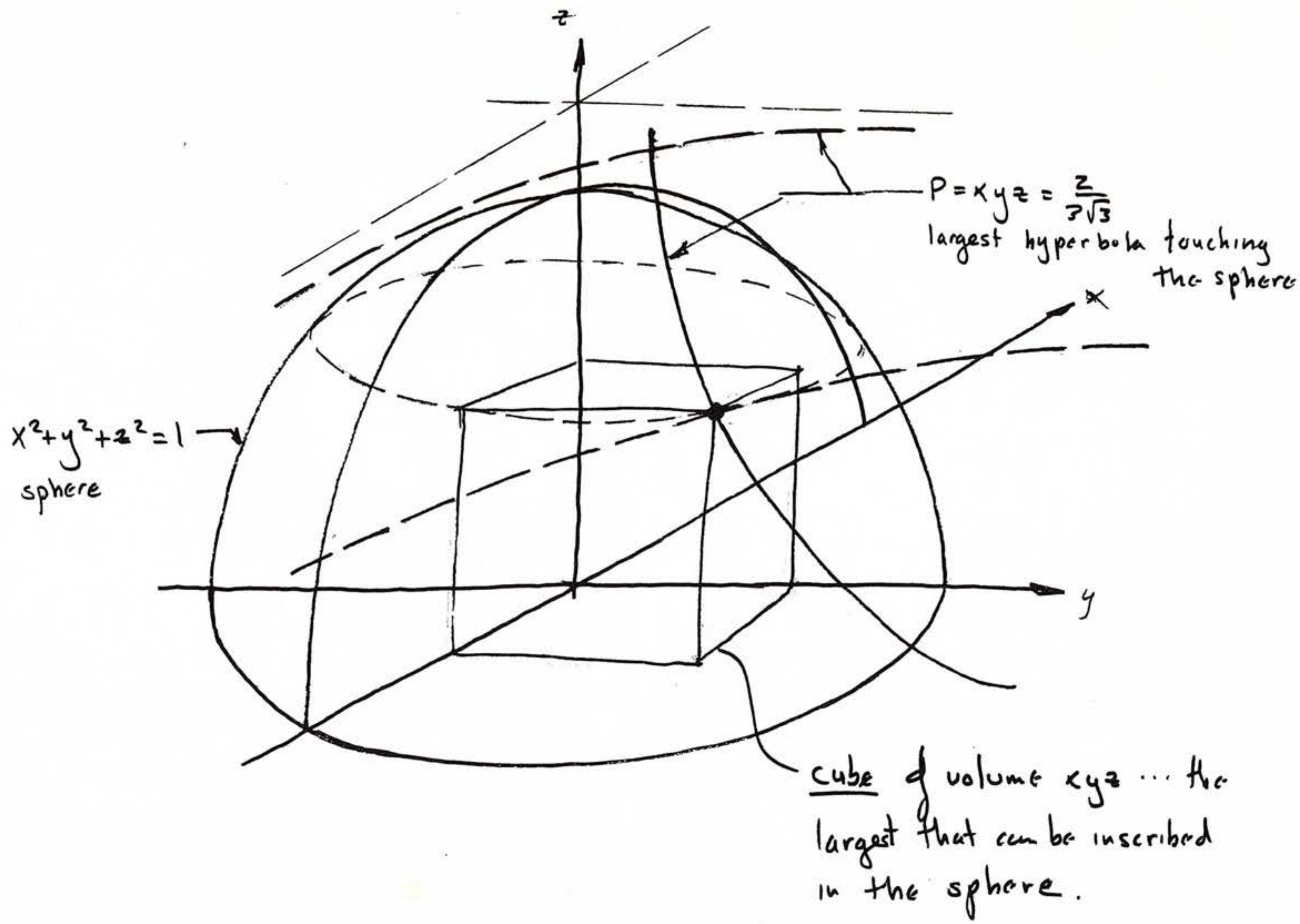
$$\left.\begin{aligned} C_m D + C_m L + 2C_w + \alpha 2 L D &= 0 \\ C_m D + \frac{C_w}{\pi} + \alpha D^2 &= 0 \end{aligned}\right\} \qquad \alpha = -\frac{C_m}{D} - \frac{C_w}{\pi D^2}$$

$$L = \frac{C_m D + 2C_w}{C_m + \frac{2C_w}{\pi D}}$$

Check: $\lim_{C_w \to 0} L = D$ ✓

B.2 The sketch should show the locus of high points on the lines of intersection between the sphere, $x^2+y^2+z^2=1$ and the rectangular hyperboloids, $8xyz = \text{Const.}$. The locus will reach its extremum where the last hyperboloid touches the sphere.

(an example is attached)


z
$P = xyz = \frac{2}{3\sqrt{3}}$
largest hyperbola touching the sphere
x
$x^2+y^2+z^2=1$
sphere
y
cube of volume xyz ... the largest that can be inscribed in the sphere.

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