28) Consider 2D gas of N-spin ½ fermions with Area = A.

$$\varepsilon(k) = \hbar v_0 |\vec{k}|$$

a) Calculate $\mu(T=0) = \varepsilon_F$.

$$\varepsilon_F = \varepsilon(k_F) = \hbar v_0 |k_F|$$

$$N = \int_0^\infty d^2k\, g(k) \frac{1}{e^{(\varepsilon-\mu)\beta}+1}$$

From HW#6: $d^2k\, g(k) = \frac{L^2}{2\pi} k\,dk = \frac{A}{2\pi} k\,dk$

extra 2 factor due to spin

$$N = 2\int_0^{k_F} dk \frac{A}{2\pi} k(1) + \int_{k_F}^\infty 0$$

$$N \overset{!}{=} 2\frac{A}{2\pi}\frac{k_F^2}{2}$$

$$k_F = \sqrt{\frac{2\pi N}{A}}$$

then $\varepsilon_F = \hbar v_0 k_F$

$$\boxed{\varepsilon_F \overset{!}{=} \hbar v_0 \sqrt{\frac{2\pi N}{A}}}$$

b) Use Sommerfield expansion to derive analytic formulae valid to lowest nonzero order in T for chemical potential μ, and const Area heat capacity C_A

$$I(T) = \int_0^\infty d\varepsilon\, \underbrace{g(\varepsilon)\, h(\varepsilon)}_{\phi(\varepsilon)}\, \underbrace{\langle n(\varepsilon)\rangle}_{f(\varepsilon)} = \int_0^\infty d\varepsilon\, \phi(\varepsilon) f(\varepsilon)$$

$$= \cancel{\Phi(\varepsilon) f \Big|_0^\infty} - \int_0^\infty d\varepsilon\, \Phi(\varepsilon) \frac{\partial f}{\partial \varepsilon}$$

where $\Phi(\varepsilon) = \int_0^\varepsilon \phi(\varepsilon')\, d\varepsilon'$

let $x = \beta(\varepsilon - \mu) \Rightarrow d\varepsilon = \frac{1}{\beta} dx$

then

$$\frac{\partial f}{\partial \varepsilon} = \frac{\partial}{\partial \varepsilon}\left(\frac{1}{e^{\beta(\varepsilon-\mu)}+1}\right) = -\beta \frac{e^x}{(e^x+1)^2}$$

$$I(T) = \int_0^\infty \Phi(\varepsilon)\, \beta \frac{e^x}{(e^x+1)^2}\, d\varepsilon$$

$$= \int_0^\infty \beta \frac{e^x}{(e^x+1)^2}\, \Phi(\varepsilon = \mu)\, d\varepsilon + \cancelto{0}{\int_0^\infty \beta \frac{e^x}{(e^x+1)^2} \frac{\partial \Phi}{\partial \varepsilon}\Big|_\mu (\varepsilon - \mu)\, d\varepsilon}$$

$$+ \int_0^\infty \beta \frac{e^x}{(e^x+1)^2} \frac{1}{2} \frac{\partial^2 \Phi}{\partial \varepsilon^2}\Big|_\mu (\varepsilon-\mu)\, d\varepsilon$$

$$= \Phi(\varepsilon=\mu) + \frac{1}{2} \frac{\partial^2 \Phi}{\partial \varepsilon^2}\Big|_\mu \underbrace{\int_0^\infty \beta \frac{e^x}{(e^x+1)^2} (\varepsilon-\mu)^2\, d\varepsilon}_{\int_{-\infty}^{\infty} \cancel{\beta} \frac{e^x}{(e^x+1)^2} x^2 \frac{1}{\beta^2} \frac{1}{\cancel{\beta}} dx}$$

$$I(T) \overset{!}{=} \Phi(\varepsilon = \mu) + \cancel{\frac{1}{2}} \frac{\partial^2 \Phi}{\partial \varepsilon^2}\Big|_{\varepsilon_F} \beta^2 \frac{\pi^2}{6} \cancel{(2)}$$

$$\overset{!}{=} \int_0^{\mu} d\varepsilon\, \phi(\varepsilon) + \frac{\pi^2}{6}(k_B T)^2 \frac{\partial \phi}{\partial \varepsilon}\Big|_{\mu}$$

for $\phi = g(\varepsilon)\, h(\varepsilon)$

Find $\mu(T)$ by find $\langle N \rangle$, or $\phi = g(\varepsilon)\, 1$

Know $g(\varepsilon) d\varepsilon = g(k) dk$.

$$N = \int_0^{\mu} d\varepsilon\, g(k)\left(\frac{\partial \varepsilon}{\partial k}\right)^{-1} + \frac{\pi^2}{6}(k_B T)^2 \frac{\partial}{\partial \varepsilon}\left[g(k)\left(\frac{\partial \varepsilon}{\partial k}\right)^{-1}\right]\Bigg|_{\mu}$$

With $g(k)\left(\frac{\partial \varepsilon}{\partial k}\right)^{-1} = 2\frac{A}{2\pi} k \left(\frac{\partial}{\partial k}\hbar v_0 k\right)^{-1} = \frac{A}{\pi} k \frac{1}{\hbar v_0}$

$$\Rightarrow g(\varepsilon) \overset{!}{=} \frac{A}{\pi} \frac{\varepsilon}{(\hbar v_0)^2}$$

$$N = \int_0^{\mu} \frac{A}{\pi} \frac{1}{(\hbar v_0)^2}\, \varepsilon\, d\varepsilon + \frac{\pi^2}{6}(k_B T)^2 \frac{\partial}{\partial \varepsilon}\left(\frac{A}{\pi} \frac{\varepsilon}{(\hbar v_0)^2}\right)$$

$$\overset{!}{=} \frac{A}{\pi} \frac{1}{(\hbar v_0)^2} \frac{\mu^2}{2} + \frac{\pi^2}{6}(k_B T)^2 \frac{A}{\pi} \frac{1}{(\hbar v_0)^2}$$

$$N \overset{!}{=} \frac{A}{2\pi} \frac{1}{(\hbar v_0)^2}\left[\mu^2 + (k_B T)^2 \frac{\pi^2}{3}\right]$$

$$\underbrace{\frac{2\pi N}{A}(\hbar v_0)^2}_{\varepsilon_F{}^2 = \mu(T=0)^2} = \left[\mu^2 + (k_B T)^2 \frac{\pi^2}{3}\right]$$

$$\boxed{\begin{aligned} u &= \sqrt{\varepsilon_F{}^2 - (k_B T)^2 \frac{\pi^2}{3}} \\ u(T) &= \varepsilon_F \left(1 - \left(\frac{k_B T}{\varepsilon_F}\right)^2 \frac{\pi^2}{6}\right) \text{ for } k_B T \ll \varepsilon_F \end{aligned}}$$

Find $C_A = \left(\frac{\partial \langle E \rangle}{\partial T}\right)_A$

Find $\langle E \rangle$: $\quad \phi(\varepsilon) = g(\varepsilon)\, \varepsilon$

$$\langle E \rangle = \int_0^u d\varepsilon \, \frac{A}{\pi} \frac{\varepsilon}{(\hbar v_0)^2} \varepsilon + \frac{\pi^2}{6} (k_B T)^2 \frac{\partial}{\partial \varepsilon}\left(\frac{A}{\pi} \frac{\varepsilon}{(\hbar v_0)^2} \varepsilon\right)\Bigg|_u$$

$$\overset{!}{=} \frac{A}{\pi} \frac{1}{(\hbar v_0)^2} \frac{u^3}{3} + \frac{\pi^2}{6} (k_B T)^2 \frac{A}{\pi} \frac{1}{(\hbar v_0)^2} 2u$$

$$\overset{!}{=} \frac{A}{2\pi (\hbar v_0)^2} \left(\frac{2u^3}{3} + \frac{2}{3} \pi^2 (k_B T)^2 u \right)$$

$$\langle E \rangle \overset{!}{=} N \frac{1}{\varepsilon_F{}^2} \frac{2}{3} u \left(u^2 + \pi^2 (k_B T)^2 \right)$$

$$\left(\frac{\partial \langle E \rangle}{\partial T}\right)_A = N \frac{1}{\varepsilon_F{}^2} \frac{2}{3} u \, 2\pi^2 k_B^2 T$$

$$\overset{!}{=} N \frac{4}{3} \pi^2 k_B \frac{\cancel{\varepsilon_F}\left(1 - \left(\frac{k_B T}{\varepsilon_F}\right)^2 \frac{\pi^2}{6}\right)}{\varepsilon_F{}^{\cancel{2}}} k_B T$$

$$\boxed{C_A = \left(\frac{\partial \langle E \rangle}{\partial T}\right)_A \overset{!}{=} N \frac{4}{3} \pi^2 k_B \left(1 - \left(\frac{k_B T}{\varepsilon_F}\right)^2 \frac{\pi^2}{6}\right) \left(\frac{k_B T}{\varepsilon_F}\right)}$$ for $k_B T \ll \varepsilon_F$

c) $I(T) = \int_0^\infty g(k) \frac{1}{e^{\beta(\varepsilon-\mu)}+1} d\varepsilon$

$$\stackrel{!}{=} \int_0^\infty \frac{A}{\pi} \frac{\varepsilon}{(\hbar v_0)^2} \frac{1}{e^{\beta(\varepsilon-\mu)}+1} d\varepsilon$$

$$\stackrel{!}{=} \int_0^\infty \frac{A}{2\pi(\hbar v_0)^2} 2\varepsilon \frac{1}{e^{\beta(\varepsilon-\mu)}+1} d\varepsilon$$

$$\cancel{N} \stackrel{!}{=} \frac{2\cancel{N}}{\varepsilon_F^2} \int_0^\infty \frac{\varepsilon}{e^{\beta(\varepsilon-\mu)}+1} d\varepsilon$$

$$1 = \frac{2}{\varepsilon_F^2} \int_0^\infty \frac{\varepsilon}{e^{\beta(\varepsilon-\mu)}+1} d\varepsilon \qquad \text{let } X = \frac{k_BT}{\varepsilon_F},\ z = \frac{\varepsilon}{\varepsilon_F}$$

$$1 \stackrel{!}{=} 2\int_0^\infty \frac{z}{\exp\{\frac{\varepsilon_F}{k_BT}(\frac{\varepsilon}{\varepsilon_F} - \frac{\mu}{\varepsilon_F})\}+1} dz$$

$$1 - 2\int_0^\infty \frac{z}{\exp\{\frac{1}{X}(z-Y)\}+1} dz = 0 \qquad \text{let } Y = \frac{\mu}{\varepsilon_F}$$

↳ Choose for a given $X = \frac{k_BT}{\varepsilon_F}$, choose Y such that equation above is zero.

Now get $\langle E \rangle = \int_0^\infty g(k)\, \varepsilon \frac{1}{e^{\beta(\varepsilon-\mu)}+1} d\varepsilon$, plug in μ that we solved before.

$$\stackrel{!}{=} \int_0^\infty \frac{2N}{\varepsilon_F^2} \frac{\varepsilon^2}{e^{\beta(\varepsilon-\mu)}+1} d\varepsilon$$

$$\stackrel{!}{=} 2N \int_0^\infty \frac{z^2}{\exp\{\frac{1}{X}(z-y)\}+1} dz\ \varepsilon_F$$

then $$\frac{\langle E \rangle}{Nk_B} = 2\int_0^\infty \frac{z^2}{\exp\{\frac{1}{x}(z-y)\}+1} dz \, \frac{\varepsilon_F}{k_B}$$

Find $\langle E \rangle' = \frac{\langle E \rangle}{Nk_B} = 2\int_0^\infty \frac{\varepsilon_F}{k_B} \frac{z^2}{\exp\{\frac{1}{x}(z-y)\}+1} dz$

$$\frac{\partial \langle E \rangle'}{\partial x} = \frac{\partial \langle E \rangle'}{\partial T} \frac{k_B}{\varepsilon_F} = \frac{\partial}{\partial T} 2\int_0^\infty \frac{z^2}{\exp\{\frac{1}{x}(z-y)\}+1} dz$$

In classical limit.

$$\mu = -k_B T \ln\left(\frac{q_1}{N}\right)$$

$$q_1 = \sum e^{-\beta\varepsilon} = \int_0^\infty g(\varepsilon)\, e^{-\beta\varepsilon}\, d\varepsilon$$

$$\overset{!}{=} \int_0^\infty \frac{A}{\pi}\frac{\varepsilon}{(\hbar v_0)^2} e^{-\beta\varepsilon}\, d\varepsilon$$

$$\overset{!}{=} \frac{A}{\pi}\frac{1}{(\hbar v_0)^2}\frac{1}{\beta^2}$$

$$\mu = -k_B T \ln\left(\frac{A}{2\pi(\hbar v_0)^2 N}\, 2(k_B T)^2\right)$$

$$\overset{!}{=} -k_B T \ln\left(2\left(\frac{k_B T}{\varepsilon_F}\right)^2\right)$$

$$\boxed{\mu \overset{!}{=} -k_B T\left(\ln 2 + 2\ln\left(\frac{k_B T}{\varepsilon_F}\right)\right)} \leftarrow \text{classical}$$

or $$\frac{\mu}{\varepsilon_F} = -\frac{k_B T}{\varepsilon_F}\left(\ln 2 + 2\ln\left(\frac{k_B T}{\varepsilon_F}\right)\right)$$

$$\langle E\rangle = \left(-\frac{\partial}{\partial\beta}\ln Q\right)_{N,A} = -\frac{\partial}{\partial\beta}\ln\left(\frac{1}{N!}q_1^N\right)$$

$$\overset{!}{=} -\frac{\partial}{\partial\beta} N\ln q_1$$

$$\overset{!}{=} -\frac{\partial}{\partial\beta} N\ln\left(\frac{A}{\pi}\frac{1}{(\hbar v_0)^2}\frac{1}{\beta^2}\right)$$

$$\overset{!}{=} 2N\beta^2\beta^{-3} = 2Nk_B T$$

$$C_A = \left(\frac{\partial\langle E\rangle}{\partial T}\right)_A = 2Nk_B$$

$$\boxed{\frac{C_A}{Nk_B} = 2}$$

we see answers match well with classical limit.

29) Charge Screening in Various Media:

dielectric: $\phi(r) = \frac{1}{4\pi\epsilon}\frac{Ze}{r}$ where $\epsilon = \epsilon_0(1+\chi_e)$

a) Consider the case where mobile carriers are quantum degenerate gas of non-interacting electrons, counter balanced by a smooth background of positive charge with charge density $\eta^{(0)} = +e\rho^{(0)}$

Thomas - Fermi method: $\mu(r) = \varepsilon_F[\rho(r)] - e\phi(r)$

$$\mu(r) = \frac{\hbar^2}{2m_e}\left(3\pi^2\rho(r)\right)^{2/3} - \frac{1}{4\pi\epsilon_0}\frac{+Ze^2}{r}e^{-K_F r}$$

In equilibrium, $\mu = \mu_0 = \text{const}$.

$\phi(r)$ must satisfy $\nabla^2\phi(r) = \frac{-\rho^{(0)}e}{\varepsilon_0}$

Show the screened electrostatic potential of the ion:

$$\phi(r) = \frac{1}{4\pi\epsilon_0}\frac{+Ze}{r}e^{-K_F r}$$

determine $K_F[\rho^{(0)}]$

First need to satisfy Poisson Eqn:

$$\nabla^2 \phi(r) = -\frac{\eta}{\varepsilon_0}$$

background positive charge

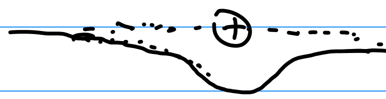
for $\eta(r) = \underset{\text{electron gas}}{-\rho e} + \underset{\text{ion at origin}}{Ze\,\delta(r)} + \rho^{(0)} e$

$$\nabla^2 \phi(r) = \frac{-Ze\,\delta(r)}{\varepsilon_0} + e\underbrace{\left(\rho(r) - \rho^{(0)}\right)}_{\delta\rho}$$

$\delta\rho \leftarrow$ have $\delta\rho$ near $r \sim 0$

Now consider small perturbation caused by ion.

$$\nabla^2 \phi(r) = \frac{-Ze\,\delta(r)}{\varepsilon_0} + \frac{\delta\rho\, e}{\varepsilon_0}$$



Use chemical potential is constant:

$$\underset{\text{const}}{\mu} = \varepsilon_F[\rho(r)] - e\phi(r)$$

$$\mu = \mu_0 + \delta\mu = \varepsilon_F[\rho^{(0)}] + \frac{\partial \varepsilon_F}{\partial \rho}\Big|_{\rho^{(0)}} \underbrace{(\rho - \rho^{(0)})}_{\delta\rho} - e\phi(r)$$

small, first order.

Compare first order terms

$$\frac{\partial \varepsilon_F}{\partial \rho}\Big|_{\rho^{(0)}} \delta\rho - e\phi = \delta\mu \cong 0$$

Since $\varepsilon_F = \left(\frac{\hbar^2}{2m_e}\right)\left(3\pi^2 \rho\right)^{2/3} = \alpha \rho^{2/3}$

$$\frac{\partial \varepsilon_F}{\partial \rho}\Big|_{\rho = \rho^{(0)}} = \frac{2}{3}\alpha \rho^{(0)^{-1/3}}$$

$$\hookrightarrow \left.\frac{\partial \varepsilon_F}{\partial \rho}\right|_{\rho=\rho^0} \delta\rho - e\,\delta\phi = 0$$

$$\hookrightarrow \delta\rho = \left(\left.\frac{\partial \varepsilon_F}{\partial \rho}\right|_{\rho=\rho^0}\right)^{-1} e\phi$$

$$\hookrightarrow \delta\rho \doteq \frac{3}{2}\alpha^{-1} \rho^{(0)\,1/3} e\phi \qquad \text{with } \alpha = \left(\frac{\hbar^2}{2m_e}\right)\left(3\pi^2\right)^{2/3}$$

then $$\nabla^2\phi(r) = \frac{-Ze\,\delta(r)}{\varepsilon_0} + \frac{\frac{3}{2}e^2\alpha^{-1}\rho^{(0)\,1/3}}{\varepsilon_0}\,\delta\phi$$

Try given ansatz $\phi(r) = \frac{+Ze}{4\pi\epsilon_0}\frac{1}{r}e^{-k_F r}$ as hinted by problem

$$\nabla^2\phi(r) = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\frac{1}{r}e^{-k_F r}\right)\frac{Ze}{4\pi\epsilon_0}$$

$$\doteq \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\left(\frac{-1}{r^2}e^{-k_F r} - \frac{k_F}{r}e^{-k_F r}\right)\right)\frac{Ze}{4\pi\epsilon_0}$$

$$\doteq \frac{1}{r^2}\left(\cancel{k_F e^{-k_F r} - k_F e^{-k_F r}} + r k_F^2 e^{-k_F r}\right)\frac{Ze}{4\pi\epsilon_0}$$

$$\doteq k_F^2\frac{1}{r}\frac{Ze}{4\pi\epsilon_0}e^{-k_F r}$$

$$\doteq k_F^2\,\phi(r)$$

By matching, we see that $k_F^2 = \frac{3e^2\alpha^{-1}\rho^{(0)\,1/3}}{2\varepsilon_0}$

$$k_F^2 = \frac{3}{\cancel{2}}\frac{\cancel{2}m_e e^2\rho^{(0)\,1/3}}{(3\pi^2)^{2/3}\hbar^2\varepsilon_0} \Rightarrow k_F = \sqrt{\frac{3m_e e^2(\rho^{(0)})^{1/3}}{(3\pi^2)^{2/3}\hbar^2\varepsilon_0}}$$

with $$\phi(r) = \frac{+Ze}{4\pi\epsilon_0}\frac{1}{r}e^{-k_F r}$$

b) Consider an electrolytic solution of positive and negative ions.

Positive: $\rho_+^{(0)}$ and ion charge $z_+ e$

Negative: $\rho_-^{(0)}$ and ion charge $-|z_-|e$

For charge neutrality: $\rho_+^{(0)} + \rho_-^{(0)} = 0$

Assume # density follow Boltzmann Distribution via total electrostatic potential $\phi(r)$:

$$\rho_+(\vec{r}) = \rho_+^{(0)} e^{-\beta e z_+ \phi(\vec{r})}$$

$$\rho_-(\vec{r}) = \rho_-^{(0)} e^{-\beta e z_- \phi(\vec{r})}$$

with Poisson Eq:

$$\nabla^2 \phi(\vec{r}) = -\frac{\eta(\vec{r})}{\varepsilon} = -\frac{+ez_+\rho_+(\vec{r}) + ez_-\rho_-(\vec{r})}{\epsilon}$$

Consider $k_B T \gg |z_\pm| e \phi$, and potential of $+Ze$ at the origin

Show $\phi(r) = \frac{1}{4\pi\epsilon} \frac{+Ze}{r} e^{-\kappa_D r}$

$$\kappa_D^2 = \frac{e^2}{\epsilon k_B T}\left[z_+^2 \rho_+^{(0)} + z_-^2 \rho_-^{(0)}\right]$$

$\Rightarrow$ With $k_BT \gg |z_\pm| e\phi \Rightarrow \dfrac{|z_\pm|e\phi}{k_BT} \ll 1$

$$\rho_\pm = \rho_\pm^{(0)} \exp\left\{-\frac{e z_\pm \phi(r)}{k_B T}\right\}$$

$$\cong \rho_\pm^{(0)}\left(1 - \frac{e z_\pm \phi(r)}{k_B T}\right)$$

Taylor

then:

ion contribution

$$\nabla^2\phi(r) = \frac{-Ze\delta(r)}{\epsilon} - \frac{e z_+ \rho_+^{(0)}\left(1 - \frac{e z_+ \phi(r)}{k_B T}\right) + e z_- \rho_-^{(0)}\left(1 - \frac{e z_- \phi(r)}{k_B T}\right)}{\epsilon}$$

$$= \frac{-Ze\delta(r)}{\epsilon} - \frac{e}{\epsilon}\left\{\underbrace{z_+\rho_+^{(0)} + z_-\rho_-^{(0)}}_{=0 \text{ due to charge neutrality}} - \left(\frac{e z_+^2 \rho_+^{(0)}}{k_B T} + \frac{e z_-^2 \rho_-^{(0)}}{k_B T}\right)\phi(r)\right\}$$

$$\boxed{\nabla^2\phi = \frac{-Ze\delta(r)}{\epsilon} + \underbrace{\frac{e^2}{\epsilon k_B T}\left(z_+^2 \rho_+^{(0)} + z_-^2 \rho_-^{(0)}\right)}_{=\kappa_D^2}\phi(r)}$$

we see that it is the same equation as part a)

so $\phi(r) = \dfrac{1}{4\pi\epsilon}\dfrac{+Ze}{r} e^{-\kappa_D r}$ is the solution

with
$$\kappa_D^2 = \frac{e^2}{\epsilon k_B T}\left(z_+^2\rho_+^{(0)} + z_-^2\rho_-^{(0)}\right)$$

30) The Activity of Ions in solution

Chemical Equilibrium Condition:

$$\prod_i \lambda_i^{\nu_i} = 1 \qquad \text{where } \lambda_i = e^{\beta \mu_i}$$

For chemist: $\mu = \mu^0(T) + k_B T \ln\left(\gamma \frac{\rho}{\rho^0(T)}\right)$ — Standard state ref concentration

Activity Coefficient: $\gamma(\rho_i, T)$

with $\mu = \left(\frac{\partial A}{\partial N_\pm}\right)_{T,V}$ $\qquad A = A_{\text{non-interacting}} + A_{el}$

$$k_B T \ln(\gamma_\pm) = \left(\frac{\partial A_{el}}{\partial N_\pm}\right)_{T,V}$$

To find A, start by finding $\langle E_{el} \rangle$. First, consider 1 ion with $+ez_+$ at $\vec{r}_1$, with other ions with net free charge $\eta(r)$.

$$E_{1+} = \int d^3r \frac{z_+ e\eta(r)}{4\pi\epsilon|\vec{r}_1 - \vec{r}|} = \int_0^\infty 4\pi r^2 dr \frac{z_+ e\eta(r)}{4\pi\epsilon r}$$

a) Why is it safe to take integral out to $r = \infty$

This because we found $\eta(r) \propto \frac{1}{r} e^{-\kappa_D r}$, so the integrand goes $\cancel{r^2} \frac{1}{\cancel{r^2}} e^{-\kappa_D r}$. The integrand decays exponentially so it practically reaches 0 as the integrand goes outside of solution, so as $r \to \infty$, there is negligible contribution.

b) Show in high temperature limit, $\frac{ze\phi}{k_BT} \ll 1$

$$E_{1+} = -\frac{z_+^2 e^2 \kappa_D}{4\pi\epsilon}$$

$\Rightarrow$ From problem 29 b), with condition $\frac{ze\phi}{k_BT} \ll 1$

we found $\eta(r) = -\epsilon \kappa_D^2 \phi = -\frac{e^2}{k_BT}\left(z_+^2 \rho_+^{(0)} + z_-^2 \rho_-^{(0)}\right)\phi$

Eq 30.5 $\quad E_{1+} = \int_0^\infty 4\pi r^2 dr \, \frac{z_+ e \eta(r)}{r}$

$$= \int_0^\infty \cancel{4\pi} r^2 dr \, \frac{z_+ e}{\cancel{4\pi} \cancel{\epsilon} r} (-\cancel{\epsilon}) \kappa_D^2 \phi(r)$$

we also found $\phi(r) = \frac{1}{4\pi\epsilon} \frac{z_+ e}{r} e^{-\kappa_D r}$ in problem 29 b)
replacing z with z_+

then $E_{1+} = \int_0^\infty -\cancel{r^2} dr \frac{(z_+ e)^2}{\cancel{r^2}} \kappa_D^2 \frac{e^{-\kappa_D r}}{4\pi\epsilon}$

$$= -\frac{(z_+ e)^2 \kappa_D^{\cancel{2}}}{4\pi\epsilon} \left(\frac{1}{-\cancel{\kappa_D}}\right) \underbrace{e^{-\kappa_D r}\Big|_0^\infty}_{(\underbrace{\cancel{e^{-\infty}}}_{0} - 1)}$$

$$\boxed{E_{1+} = -\frac{(z_+ e)^2 \kappa_D}{4\pi\epsilon}}$$

c) Show $\langle E_{el} \rangle = \frac{1}{2} \sum N_i E_i = -\frac{V k_B T \kappa_D^3}{8\pi}$

$$\langle E_{el} \rangle = \frac{1}{2} \sum_i N_i E_i$$

$$= \frac{1}{2} V \left(\rho_+^{(0)} E_+ + \rho_-^{(0)} E_- \right)$$

From part b)

$$E_{1+} = -\frac{z_+^2 e^2 \kappa_D}{4\pi\epsilon} \quad , \text{ similarly } \quad E_{1-} = -\frac{z_-^2 e^2 \kappa_D}{4\pi\epsilon}$$

$$\langle E_{el} \rangle = \frac{1}{2} V \left[\rho_+^{(0)} \left(\frac{-z_+^2 e^2}{4\pi\epsilon} \right) \kappa_D + \rho_-^{(0)} \left(\frac{-z_-^2 e^2}{4\pi\epsilon} \right) \kappa_D \right]$$

$$= -\frac{V}{8\pi} \kappa_D \left(\underbrace{\frac{e^2}{\epsilon} \left[z_+^2 \rho_+^{(0)} + z_-^2 \rho_-^{(0)} \right]}_{} \right)$$

recognize $= \kappa_D^2 k_B T$

$$\boxed{\langle E_{el} \rangle = -\frac{V k_B T \kappa_D^3}{8\pi}}$$

d) Show $A_{el} = \frac{-V k_B T \kappa_D^3}{12\pi}$

satisfies Gibbs-Helmholtz equation:

$$\left(\frac{\partial(A_{el}/T)}{\partial T}\right)_{V,N} = \frac{-\langle E_{el}\rangle}{T^2}$$

$$\Rightarrow A_{el} = -\frac{V k_B T}{12\pi}\left(\frac{e^2}{\epsilon}\left[z_+^2 \rho_+^{(0)} + z_-^2 \rho_-^{(0)}\right]\frac{1}{k_B T}\right)^{3/2}$$

$$= -\frac{V}{12\pi}\left(\frac{e^2}{\epsilon}\left[z_+^2 \rho_+^{(0)} + z_-^2 \rho_-^{(0)}\right]\right)^{3/2}\frac{1}{\sqrt{k_B T}}$$

then $$\frac{A_{el}}{T} = -\frac{V}{12\pi}\left(\frac{e^2}{\epsilon}\left[z_+^2 \rho_+^{(0)} + z_-^2 \rho_-^{(0)}\right]\right)^{3/2}\frac{1}{\sqrt{k_B}}\frac{1}{T^{3/2}}$$

then $$\left(\frac{\partial(A_{el}/T)}{\partial T}\right)_{V,N} = \frac{3}{2}\frac{V}{12\pi}\left(\frac{e^2}{\epsilon}\left[z_+^2 \rho_+^{(0)} + z_-^2 \rho_-^{(0)}\right]\right)^{3/2}\frac{1}{\sqrt{k_B}}\frac{1}{T^{5/2}}$$

$$= \underbrace{\frac{V k_B T}{8\pi}\left(\frac{e^2}{\epsilon}\left[z_+^2 \rho_+^{(0)} + z_-^2 \rho_-^{(0)}\right]\right)^{3/2}\frac{1}{(k_B T)^{3/2}}}_{= -\langle E_{el}\rangle}\frac{1}{T^2}$$

$$\boxed{\left(\frac{\partial(A_{el}/T)}{\partial T}\right)_{V,N} = -\frac{\langle E_{el}\rangle}{T^2}}$$

e) Derive an expression for $\gamma_\pm$. Discuss Result
→ what happens as ion concentration → 0.
→ What happens as $T \to \infty$.
→ Do they make sense.

$$k_B T \ln \gamma_\pm = \left(\frac{\partial A_{el}}{\partial N_\pm}\right)_{T,V}$$

$$\text{or} \quad \gamma_\pm = \exp\left\{\frac{1}{k_B T}\left(\frac{\partial A_{el}}{\partial N_\pm}\right)_{T,V}\right\}$$

$$\left(\frac{\partial A_{el}}{\partial N_\pm}\right)_{T,V} = \left(\frac{\partial A_{el}}{\partial \rho_\pm}\right)_{T,V}\left(\frac{d\rho_\pm}{dN_\pm}\right)_{T,V} \qquad \rho_\pm = \frac{N_\pm}{V} \Rightarrow \left(\frac{d\rho}{dN_\pm}\right)_{T,V} = \frac{1}{V}$$

$$\stackrel{!}{=} \frac{1}{\cancel{V}}\left\{\frac{\partial}{\partial \rho_\pm} - \frac{\cancel{V} k_B T}{12\pi}\left(\frac{e^2}{\epsilon k_B T}\left[z_+^2 \rho_+^{(0)} + z_-^2 \rho_-^{(0)}\right]\right)^{3/2}\right\}_{T,V}$$

$$\left(\frac{\partial A_{el}}{\partial N_\pm}\right)_{T,V} \stackrel{!}{=} -\frac{k_B T}{12\pi}\left(\frac{e^2}{\epsilon k_B T}\right)^{3/2} \frac{3}{2}\left[z_+^2 \rho_+^{(0)} + z_-^2 \rho_-^{(0)}\right]^{1/2} z_\pm^2$$

$$\text{then} \quad \gamma_\pm = \exp\left\{\frac{1}{k_B T}\left(\frac{\partial A_{el}}{\partial N_\pm}\right)_{T,V}\right\}$$

$$\gamma_\pm \stackrel{!}{=} \exp\left\{-\frac{1}{8\pi}\left(\frac{e^2}{\epsilon k_B T}\right)^{3/2}\left[z_+^2 \rho_+^{(0)} + z_-^2 \rho_-^{(0)}\right]^{1/2} z_\pm^2\right\}$$

$$\text{let} \quad \kappa_D = \sqrt{\frac{e^2}{\epsilon k_B T}\left[z_+^2 \rho_+^{(0)} + z_-^2 \rho_-^{(0)}\right]}$$

$$\boxed{\gamma_\pm \stackrel{!}{=} \exp\left\{-\frac{1}{8\pi}\frac{z_\pm^2 e^2}{\epsilon k_B T}\kappa_D\right\}}$$

$\Rightarrow$ As $\rho_+^{(0)} = \rho_-^{(0)} = 0$, we see

$$\gamma_\pm = \exp\{0\} = 1$$

We see that it goes to ideal gas solution which make sense since now there is no electrostatic interactions.

$\Rightarrow$ As $T \to \infty$

$$\gamma_\pm = \exp\left\{-\frac{1}{\infty}\right\} = 1$$

we again approach ideal gas, this also make sense since temperature is a measure of average thermal energy that the particle experiences, as $T \to \infty$, particles have so much kinetic energy such that the electrostatic contribution becomes neglible.

f) Plot $\lambda_D = 1/\kappa_D$ and $\gamma_\pm$ vs. concentration from 0 to 0.1 mol/liter at 25°C. for NaCl dissolved in water. $\epsilon/\epsilon_0 = 78.54$

Suppose we have concentration C of NaCl, since Na^+ and Cl^-, with corresponding $z_+ = 1, z_- = -1$, then

$$\kappa_D = \sqrt{\frac{e^2}{\epsilon k_B T}\left[\underbrace{\rho_+^{(0)} + \rho_-^{(0)}}\right]} = \sqrt{\frac{e^2}{\epsilon k_B T} 2\rho_{NaCl}}$$

and

$$\gamma_\pm = \exp\left\{\frac{-1}{8\pi}\frac{e^2}{\epsilon k_B T}\kappa_D\right\}$$