Spring 2003 Physics 603 O. W. Greenberg

Solutions to homework due 4/8/03

Assignment 6

6.1. We start with eqn. (6.1.19) and write it in the form

$$S = k\sum_i \left[n_i^* \ell n\left(\frac{g_i}{n_i^*}\right) + \left(n_i^* - \frac{g_i}{a}\right)\ell n\left(1 - a\frac{n_i^*}{g_i}\right)\right] . \tag{1}$$

Now, setting all $g_i = 1$ and identifying (n_i^* / g_i) with $\langle n_\varepsilon \rangle$, see eqns. (6.1.18a) and (6.2.22), we get

$$S = k\sum_\varepsilon \left[-\langle n_\varepsilon \rangle \ell n \langle n_\varepsilon \rangle + \left(\langle n_\varepsilon \rangle - \frac{1}{a}\right)\ell n(1 - a\langle n_\varepsilon \rangle)\right] . \tag{2}$$

Choosing $a = -1$ or $+1$, we obtain the desired results.

Next we have to verify that

$$S = -k\sum_\varepsilon \left\{ \sum_n p_\varepsilon(n) \ell n\, p_\varepsilon(n)\right\} = -k\sum_\varepsilon \langle \ell n\, p_\varepsilon(n)\rangle . \tag{3}$$

Substituting for $p_\varepsilon(n)$ from eqn. (6.3.10) into (3) leads to the desired result (2), with $a = -1$; substituting from eqn. (6.3.11) instead leads to the desired result (2), with $a = +1$.

6.2. In the *B.E.* case, see eqn. (6.3.10),

$$p_\varepsilon(n) = (1-r)r^n \quad \left[r = \langle n_\varepsilon \rangle \Big/ \left(\langle n_\varepsilon \rangle + 1 \right);\ n = 0,1,2,\ldots \right] .$$

It follows that

$$\langle n_\varepsilon \rangle = (1-r)\sum_{n=0}^{\infty} n r^n = r/(1-r) ,$$

$$\langle n_\varepsilon^2 \rangle = (1-r)\sum_{n=0}^{\infty} n^2 r^n = r(1+r)/(1-r)^2, \text{ so that}$$

$$\langle n_\varepsilon^2 \rangle - \langle n_\varepsilon \rangle^2 = r/(1-r)^2 = \langle n_\varepsilon \rangle + \langle n_\varepsilon \rangle^2 . \tag{1}$$

In the *F.D.* case, see eqn. (6.3.11),

$$\langle n_\varepsilon^2 \rangle = \sum_{n=0}^{1} n^2 p_\varepsilon(n) = p_\varepsilon(1) = \langle n_\varepsilon \rangle , \text{ so that}$$

$$\langle n_\varepsilon^2 \rangle - \langle n_\varepsilon \rangle^2 = \langle n_\varepsilon \rangle - \langle n_\varepsilon \rangle^2 . \tag{2}$$

In the *M.B.* case, see eqn. (6.3.12), one can readily see that

$$\langle n_\varepsilon(n_\varepsilon - 1)\rangle = \sum_n n(n-1)\frac{\langle n_\varepsilon \rangle^n}{n!}e^{-\langle n_\varepsilon \rangle} = \langle n_\varepsilon \rangle^2 \sum_n \frac{\langle n_\varepsilon \rangle^{n-2}}{(n-2)!}e^{-\langle n_\varepsilon \rangle} = \langle n_\varepsilon \rangle^2, \text{ so that}$$

$$\langle n_\varepsilon^2 \rangle - \langle n_\varepsilon \rangle^2 = \langle n_\varepsilon \rangle . \tag{3}$$

For the second part, we note, from eqn. 6.2.22, that

$$\langle n_\varepsilon \rangle^{-1} = e^{(\varepsilon-\mu)/kT} + a \ .$$

Differentiating this result with respect to μ, we get

$$-\langle n_\varepsilon \rangle^{-2}\left[\frac{\partial\langle n_\varepsilon\rangle}{\partial\mu}\right]_T = -\frac{1}{kT}e^{(\varepsilon-\mu)/kT} = -\frac{1}{kT}\left[\langle n_\varepsilon\rangle^{-1} - a\right] \ .$$

It follows that

$$kT\left[\frac{\partial\langle n_\varepsilon\rangle}{\partial\mu}\right]_T = \langle n_\varepsilon\rangle - a\langle n_\varepsilon\rangle^2 \ . \tag{4}$$

Comparing (4) with our previous results (1)-(3), and with formula (6.3.9), we infer that, quite generally,

$$\langle n_\varepsilon^2\rangle - \langle n_\varepsilon\rangle^2 = kT\left[\partial\langle n_\varepsilon\rangle / \partial\mu\right]_T \ .$$

<u>6.3.</u> Starting with eqn. (6.2.15), we now have

$$\mathcal{Q}(z,V,T) = \prod_\varepsilon\left[\sum_{n_\varepsilon=0}^{\ell}(z\,e^{-\beta\varepsilon})^{n_\varepsilon}\right] = \prod_\varepsilon\left[\frac{1-(ze^{-\beta\varepsilon})^{\ell+1}}{1-z\,e^{-\beta\varepsilon}}\right],$$

so that

$$q(z,V,T) = \sum_\varepsilon\left[\ell n\left\{1-(z\,e^{-\beta\varepsilon})^{\ell+1}\right\} - \ell n\left\{1-z\,e^{-\beta\varepsilon}\right\}\right];$$

cf. eqn. (6.2.17). It follows that

$$\begin{aligned}\langle n_\varepsilon\rangle &= -\frac{1}{\beta}\left(\frac{\partial q}{\partial\varepsilon}\right)_{z,T,\,\text{all other }\varepsilon}\\ &= -\frac{(\ell+1)(z\,e^{-\beta\varepsilon})^{\ell}(z\,e^{-\beta\varepsilon})}{1-(ze^{-\beta\varepsilon})^{\ell+1}} + \frac{z\,e^{-\beta\varepsilon}}{1-z\,e^{-\beta\varepsilon}}\\ &= \frac{1}{z^{-1}e^{\beta\varepsilon}-1} - \frac{\ell+1}{(z^{-1}e^{\beta\varepsilon})^{\ell+1}-1} \ .\end{aligned}$$

For $\ell = 1$, we obtain the Fermi-Dirac result; for $\ell \to \infty$ and $z^{-1}e^{\beta\varepsilon} > 1$ [see eqn. (6.2.16a)], we obtain the Bose-Einstein result.

6.4. To determine the state of equilibrium of the given system, we minimize its free energy, $U-TS$, under the constraint that the total number of particles, N, is fixed. For this, we vary the particle distribution from $n(\mathbf{r})$ to $n(\mathbf{r})+\delta n(\mathbf{r})$ and require that the resulting variation

$$\delta(U-TS)=\frac{e^2}{2}\iint\frac{n(\mathbf{r})\delta n(\mathbf{r}')+n(\mathbf{r}')\delta n(\mathbf{r})}{|\mathbf{r}-\mathbf{r}'|}\,d\mathbf{r}d\mathbf{r}'+e\int\delta n(\mathbf{r})\varphi_{ext}(\mathbf{r})d\mathbf{r}$$

$$+kT\int[1+\ell n\, n(\mathbf{r})]\delta n(\mathbf{r})\,d\mathbf{r}=0\ ,$$

while $\delta N=\int\delta n(\mathbf{r})\,d\mathbf{r}$ is, of necessity, zero. Introducing the Lagrange multiplier λ, our requirement takes the form

$$\int\left[e^2\int\frac{n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}'+e\varphi_{ext}(\mathbf{r})+kT\,[1+\ell n\, n(\mathbf{r})]-\lambda\right]\delta n(\mathbf{r})d\mathbf{r}=0\ .$$

Since the variation $\delta n(\mathbf{r})$ in this expression is arbitrary, the condition for equilibrium turns out to be

$$e^2\int\frac{n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\,d\mathbf{r}'+e\varphi_{ext}(\mathbf{r})+kT\,\ell n\, n(\mathbf{r})-\mu=0\ , \tag{1}$$

where $\mu=\lambda-kT$.

Introducing the total potential $\varphi(\mathbf{r})$, viz.

$$\varphi(\mathbf{r})=\varphi_{ext}(\mathbf{r})+e\int\frac{n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}'\ , \tag{2}$$

condition (1) takes the Boltzmannian form

$$n(\mathbf{r})=\exp[\{\mu-e\varphi(\mathbf{r})\}/kT]\ . \tag{3}$$

Choosing $n(\mathbf{r})$ to be n_0 at the point where $\varphi(\mathbf{r})=0$, eqn. (3) may be written as

$$n(\mathbf{r})=n_0\exp[-e\varphi(\mathbf{r})/kT]\ . \tag{4}$$

With $\varphi_{ext}(\mathbf{r})$ given, the coupled equations (2) and (4) together determine the desired functions $n(\mathbf{r})$ and $\varphi(\mathbf{r})$.

6.6. We have to show that, for *any* law of distribution of molecular speeds [say, $F(u)du$],

$$\frac{\int_0^\infty u\,F(u)du}{\int_0^\infty F(u)du}\cdot\frac{\int_0^\infty u^{-1}\,F(u)du}{\int_0^\infty F(u)du}\geq 1\ , \text{ i.e.}$$

$$\int_0^\infty u\,F(u)du\cdot\int_0^\infty u^{-1}\,F(u)du\geq\left[\int_0^\infty F(u)du\right]^2 .$$

For this, we employ Schwarz's inequality (see Abramowitz and Stegun, 1964),

$$\left[\int_a^b f(x)g(x)dx\right]^2\leq\int_a^b[f(x)]^2dx\cdot\int_a^b[g(x)]^2dx\ ,$$

which holds for arbitrary functions $f(x)$ and $g(x)$ —— so long as the integrals exist; the equality holds if and only if $f(x)=c\,g(x)$, where c is a constant. Now, with $f(u)=\sqrt{uF(u)}$ and $g(u)=\sqrt{u^{-1}F(u)}$, we obtain the desired result.

For the Maxwellian distribution,

$$F(u)du\sim e^{-\frac{1}{2}\beta m u^2}\,u^2du\ .$$

It is then straightforward to see, with the help of the formulae (B.13), that

$$\langle u\rangle=\frac{I_3}{I_2}=\left(\frac{8}{\pi\beta m}\right)^{1/2}\quad\text{and}\quad\langle u^{-1}\rangle=\frac{I_1}{I_2}=\left(\frac{2\beta m}{\pi}\right)^{1/2},$$

whence $\langle u\rangle\langle u^{-1}\rangle=4/\pi$, in conformity with the inequality stated.