Spring 2003 Physics 603 O. W. Greenberg

Solutions to homework due 4/1/03

5.3 (i) free particle $\hat{H} = \frac{\hat{\vec{p}}^2}{2m}$, $\langle \vec{p} | \hat{H} | \vec{p}' \rangle = \frac{\vec{p}^2}{2m} \delta_{\vec{p}, \vec{p}'} = \frac{\vec{p}^2}{2m} \delta_{\vec{n}, \vec{n}'}$

$\langle \vec{p} | e^{-\beta \hat{H}} | \vec{p}' \rangle = e^{-\beta \frac{\vec{p}^2}{2m}} \delta_{\vec{p}, \vec{p}'}$ $\qquad \vec{p} = \frac{\hbar \cdot 2\pi \vec{n}}{L}$, $\vec{p}' = \frac{\hbar \cdot 2\pi \vec{n}'}{L}$

$$Tr(e^{-\beta \hat{H}}) = \sum_{\vec{p}, \vec{p}'} e^{-\beta \frac{\vec{p}^2}{2m}} \delta_{\vec{p}, \vec{p}'} = \sum_{\vec{p}} e^{-\beta \frac{\vec{p}^2}{2m}} = \frac{V}{h^3} \int d^3p \, e^{-\beta \frac{\vec{p}^2}{2m}} =$$

$$= \frac{V}{h^3} \left(\frac{2m\pi}{\beta} \right)^{3/2} = V \left(\frac{m}{2\pi \beta \hbar^2} \right)^{\frac{3}{2}},$$ using $\frac{d^3q \, d^3p}{h^3}$ = no. of quantum states,

so $\sum_{p} \to \frac{V}{h^3} \int d^3p$

$$\langle \vec{p} | \hat{\rho} | \vec{p}' \rangle = \frac{1}{V} \left(\frac{2\pi\beta \hbar^2}{m} \right)^{3/2} e^{-\beta \frac{\vec{p}^2}{2m}} \delta_{\vec{p}, \vec{p}'}$$

(ii) linear harmonic oscillator - see next pages

Useful techniques:
The text (p114) quotes the result for $\langle q| e^{-\beta \hat{H}} |q'\rangle$, but doesn't give the derivation. As a warm up, let's calculate this directly without doing a sum of products of Hermite polynomials. Derive differential eq.'s. First introduce dimensionless variables,

$$\hat{H} = \hat{\mathcal{H}} \cdot \hbar\omega, \quad \hat{q} = \sqrt{\frac{\hbar}{m\omega}}\,\hat{Q}, \quad \hat{p} = \sqrt{m\hbar\omega}\,\hat{P}, \quad \hat{H} = \frac{\hat{p}^2}{2m} + \frac{1}{2} m\omega^2 \hat{q}^2.$$

Next introduce annihilation and creation operators,

$$a = \frac{1}{\sqrt{2}}(\hat{Q} + i\hat{P}), \quad a^{+} = \frac{1}{\sqrt{2}}(\hat{Q} - i\hat{P}); \quad \hat{Q} = \frac{a + a^{+}}{\sqrt{2}}, \quad \hat{P} = i\,\frac{a^{+} - a}{\sqrt{2}},$$

$$\hat{\mathcal{H}} = a^{+}a + \tfrac{1}{2}, \quad [\hat{\mathcal{H}}, \hat{Q}] = -i\hat{P}, \quad [\hat{\mathcal{H}}, \underbrace{[\hat{\mathcal{H}}, \hat{Q}]}_{-iP}] = Q, \quad \text{etc.}$$

Then $$e^{-\lambda \hat{\mathcal{H}}}\,\hat{Q}\,e^{\lambda \hat{\mathcal{H}}} = \hat{Q} + (-\lambda)[\hat{\mathcal{H}}, Q] + \frac{(-\lambda)^2}{2!}[\hat{\mathcal{H}}, [\hat{\mathcal{H}}, Q]] + \cdots$$

$$= \hat{Q} + i\lambda\hat{P} + \tfrac{1}{2}\lambda^2\hat{Q} + \frac{i}{3!}\lambda^3\hat{P} + \cdots = \cosh\lambda \cdot \hat{Q} + i\sinh\lambda \cdot \hat{P}$$

$$\langle q| e^{-\beta \hat{H}} |q'\rangle = \frac{\hbar}{m\omega}\langle Q| e^{-\lambda \hat{\mathcal{H}}} |Q'\rangle, \quad \lambda = \beta\hbar\omega.$$

$$\langle Q| e^{-\lambda \hat{\mathcal{H}}}\,\hat{Q}\,|Q'\rangle = Q'\langle Q| e^{-\lambda \hat{\mathcal{H}}} |Q'\rangle \quad \text{and}$$

$$\langle Q| e^{-\lambda \hat{\mathcal{H}}}\,\hat{Q}\,|Q'\rangle = \langle Q| e^{-\lambda \hat{\mathcal{H}}}\,\hat{Q}\,e^{\lambda \hat{\mathcal{H}}} e^{-\lambda \hat{\mathcal{H}}} |Q'\rangle =$$

$$= \langle Q| (\cosh\lambda \cdot \hat{Q} + i\sinh\lambda \cdot \hat{P})\, e^{-\lambda \hat{\mathcal{H}}} |Q'\rangle$$

$$= \left(Q\cosh\lambda + i\sinh\lambda \cdot i\,\frac{\partial}{\partial Q}\right)\langle Q| e^{-\lambda \hat{\mathcal{H}}} |Q'\rangle, \quad \text{using}$$

$$\hat{P}^{+} = \hat{P}, \quad \hat{P}|Q\rangle = \frac{1}{i}\frac{\partial}{\partial Q}|Q\rangle, \quad \langle Q|\hat{P} = i\frac{\partial}{\partial Q}\langle Q|.$$

So the differential eq. is

$$\left(Q\cosh\lambda - \sinh\lambda\,\frac{\partial}{\partial Q} - Q'\right)\langle Q| e^{-\lambda \hat{\mathcal{H}}} |Q'\rangle = 0$$

Try $\langle Q | e^{-\lambda \mathcal{H}} | Q' \rangle = e^{\phi(Q)} F(Q')$. Then

$$\left(Q \cosh\lambda - \sinh\lambda \cdot \phi'(Q) - Q' \right) F(Q') = 0$$

$$\phi'(Q) = Q \coth\lambda - Q' \frac{1}{\sinh\lambda}, \quad \phi(Q) = \tfrac{1}{2} Q^2 \coth\lambda - \frac{QQ'}{\sinh\lambda} + \psi(Q')$$

The analogous argument starting from

$\langle Q | \hat{Q}\, e^{-\lambda \hat{\mathcal{H}}} | Q' \rangle$ gives the differential eq.

$$\left(Q' \cosh\lambda - \sinh\lambda \frac{\partial}{\partial Q'} - Q\right) \langle Q | e^{-\lambda \hat{\mathcal{H}}} | Q' \rangle = 0$$

The $F(Q')$ in the previous ansatz is accounted for by $e^{\psi(Q')}$, so now we must solve

$$Q' \cosh\lambda - \sinh\lambda\, \psi'(Q') = 0, \quad \psi(Q') = \tfrac{1}{2} Q'^2 \coth\lambda.$$

The result is

$$\langle Q | e^{-\lambda \hat{\mathcal{H}}} | Q' \rangle = \exp\left[\tfrac{1}{2}(Q^2 + Q'^2) \coth\lambda - \frac{QQ'}{\sinh\lambda} \right]$$

when we replace Q with $\sqrt{\frac{m\omega}{\hbar}}\, q$, etc. and use hyperbolic trig formulas (or derive them as needed), we get

$$\langle q | e^{-\lambda \hat{H}} | q' \rangle = \frac{\hbar}{m\omega} \exp\left[\frac{m\omega}{4\hbar} \left\{ (q+q')^2 \tanh\frac{\beta\hbar\omega}{2} + (q-q')^2 \coth\frac{\beta\hbar\omega}{2} \right\} \right].$$

This differs from (23), p.ii by the prefactor

$\left[\dfrac{m\omega}{2\pi\hbar \sinh\beta\hbar\omega} \right]^{\frac{1}{2}}$ which will cancel when we calculate

$\langle q | \hat{\rho} | q' \rangle = \dfrac{\langle q | e^{-\beta \hat{H}} | q' \rangle}{\operatorname{tr} e^{-\beta \hat{H}}}$ and doesn't matter, and by an

overall (-1) in the exponent, which is WRONG. Challenge to the class: Find the (-1) factor.

The problem asks for $\langle p|\hat{P}|p'\rangle$. We don't want to do all the work over again using analogous arguments for $\hat{P}$. Instead, since $\hat{H} = \frac{1}{2}(\hat{Q}^2 + \hat{P}^2)$ and $[\hat{H}, \hat{Q}] = -i\hat{P}$, $[\hat{H}, \hat{P}] = i\hat{Q}$, the only difference between $\langle Q|e^{-\lambda \hat{H}}|Q'\rangle$ and $\langle P|e^{-\lambda \hat{H}}|P'\rangle$ is a possible (-1); but since the result is bilinear in Q and Q', any (-1) will square to 1. Thus

$$\langle P|e^{-\lambda \hat{H}}|P'\rangle = \exp\left[\frac{1}{2}(P^2+P'^2)\coth\lambda - \frac{PP'}{\sinh\lambda}\right] \text{ and}$$

$$\langle p|e^{-\beta \hat{H}}|p'\rangle = \frac{1}{m\hbar\omega}\exp\left[\frac{\coth\beta\hbar\omega}{2m\hbar\omega}(p^2+p'^2)^2 - \frac{pp'}{m\hbar\omega\sinh\beta\hbar\omega}\right].$$

Again there is a missing (-1) in the exponent.

In terms of $(p+p')^2$ and $(p-p')^2$ the result is

$$\langle p|e^{-\beta \hat{H}}|p'\rangle = \frac{1}{m\hbar\omega}\exp\left\{\frac{1}{4m\hbar\omega}\left[(p+p')^2\tanh\beta\frac{\hbar\omega}{2} + (p-p')\coth\beta\frac{\hbar\omega}{2}\right]\right\}$$

To get the standard normalization, require

$$\langle q|e^{-\beta \hat{H}}|q'\rangle = \delta(q-q') \text{ for } \beta \to 0.$$

Now

$$C\exp\left[\frac{m\omega}{4\hbar}(q-q')^2\frac{2}{\beta\hbar\omega}\right] \to \delta(q-q'),\ \beta\to 0$$

$$\int d(q-q')\, f(q-q')\, C\exp\Big[\underbrace{-\frac{m}{2\hbar^2\beta}(q-q')^2}_{x^2}\Big] = \sqrt{\frac{2\hbar^2\beta}{m}}\int dx\, f\Big(\sqrt{\tfrac{2\hbar^2\beta}{m}}\,x\Big)\, C e^{-x^2} \qquad x = \sqrt{\tfrac{m}{2\hbar^2\beta}}\,(q-q')$$

$$= \sqrt{\frac{2\hbar^2\beta}{m}}\, C\, f(0)\sqrt{\pi} = f(0),\quad C = \sqrt{\frac{m}{2\pi\hbar^2\beta}},$$ which

agrees with (23) on p 14 in the small β limit.

5.4. If we use the *unsymmetrized* wave function (5.4.3), rather than the *symmetrized* wave function (5.5.7), the density matrix of the system turns out to be, cf. eqn. (5.5.11),

$$\left\langle 1,\ldots,N\right|e^{-\beta\hat{H}}\left|1',\ldots,N'\right\rangle = \sum_{\mathbf{K}} e^{-\beta\hbar^2K^2/2m}\left\{u_{\mathbf{k}_1}(1)\ldots u_{\mathbf{k}_N}(N)\right\}\left\{u^*_{\mathbf{k}_1}(1')\ldots u^*_{\mathbf{k}_N}(N')\right\}$$

$$= \sum_{\mathbf{k}_1,\ldots,\mathbf{k}_N} e^{-\beta\hbar^2(k_1^2+\ldots+k_N^2)/2m}\left[\left\{u_{\mathbf{k}_1}(1)u^*_{\mathbf{k}_1}(1')\right\}\ldots\left\{u_{\mathbf{k}_N}(N)u^*_{\mathbf{k}_N}(N')\right\}\right]$$

$$= \prod_{j=1}^{N}\left[\sum_{\mathbf{k}_j} e^{-\beta\hbar^2k_j^2/2m}\left\{u_{\mathbf{k}_j}(j)u^*_{\mathbf{k}_j}(j')\right\}\right].$$

Replacing the summation over $\mathbf{k}_j$ by an integration, one gets [see the corresponding passage from eqn. (5.5.12) to (5.5.14)]

$$\left\langle 1,\ldots,N\right|e^{-\beta\hat{H}}\left|1',\ldots,N'\right\rangle = \left(\frac{m}{2\pi\beta\hbar^2}\right)^{3N/2}\exp\left\{-\frac{m}{2\beta\hbar^2}\left(\xi_1^2+\ldots+\xi_N^2\right)\right\}, \tag{1}$$

where $\xi_j = \left|\mathbf{r}_j - \mathbf{r}'_j\right|$. The diagonal elements of the density matrix then are

$$\left\langle 1,\ldots,N\right|e^{-\beta\hat{H}}\left|1,\ldots,N\right\rangle = \left(m/2\pi\beta\hbar^2\right)^{3N/2} = 1/\lambda^{3N}, \tag{2}$$

where λ is the mean thermal wavelength of the particles. The structure of expressions (1) and (2) shows that there is *no* spatial correlation among the particles of this system.

The partition function now turns out to be

$$Q_N(V,T) \equiv Tr\left(e^{-\beta\hat{H}}\right) = \int \frac{1}{\lambda^{3N}}d^{3N}r = \frac{V^N}{\lambda^{3N}},$$

with *no* Gibbs' correction factor.

5.5. By eqn. (5.5.17), we have

$$Q_N(V,T) \equiv Tr\left(e^{-\beta\hat{H}}\right) = \frac{1}{N!\lambda^{3N}}Z_N(V,T),$$

where

$$Z_N(V,T) = \int \sum_P \{\ldots\} d^{3N}r. \tag{1}$$

In the *zeroth* approximation, $\sum_P = 1$; see eqn. (5.5.19). So, $Z_N(V,T) = V^N$. In the *first* approximation,

$$\sum_P = 1 \pm \sum_{i<j} f_{ij}f_{ji} = 1 \pm \sum_{i<j} e^{-2\pi r_{ij}^2/\lambda^2}. \tag{2}$$

If λ is much smaller than the mean interparticle distance, we may write

$$\sum_P \approx \prod_{i<j}\left(1 \pm e^{-2\pi r_{ij}^2/\lambda^2}\right) = \prod_{i<j} e^{-\beta v_s(r_{ij})} = \exp\left\{-\beta\sum_{i<j} v_s(r_{ij})\right\},$$

which leads to the desired result.

For the second part, we substitute (2) into (1) and integrate over the position coordinates of the particles. We obtain, on assembling contributions from *all* pairs of particles,

$$Z_N(V,T) = V^N \pm \frac{N(N-1)}{2} \cdot V^{N-2} \frac{V \cdot \lambda^3}{2^{3/2}} .$$

The case $N = 2$ corresponds to eqn. (5.5.25) for $Q_2(V,T)$. For $N \gg 1$ and $N\lambda^3 \ll V$, we may write

$$Z_N(V,T) = V^N \left[1 \pm N^2 \frac{\lambda^3}{2^{5/2} V}\right] \approx V^N \left[1 \pm \frac{N\lambda^3}{2^{5/2} V}\right]^N .$$

It follows that

$$\ell n\, Q_N(V,T) \approx -N\,\ell n\, N + N + N\,\ell n\left(\frac{V}{\lambda^3}\right) + N\left(\pm \frac{N\lambda^3}{2^{5/2} V}\right),$$

whence

$$\frac{P}{kT} \equiv \left(\frac{\partial\, \ell n\, Q_N}{\partial V}\right)_{N,T} \approx \frac{N}{V} \mp \frac{N^2 \lambda^3}{2^{5/2} V^2} = \frac{1}{\mathrm{v}} \mp \frac{1}{2^{5/2}} \frac{\lambda^3}{\mathrm{v}^2} ,$$

where $\mathrm{v} = V/N$; cf. eqns. (7.1.13) and (8.1.17).

5.8 Prove Peierls' theorem

$\hat{H}^\dagger = \hat{H}$, $\{\phi_n\}$ orthonormal, not necessarily complete,

then $Q(\beta) = \sum_n \langle \psi_n | e^{-\beta \hat{H}} | \psi_n \rangle \geq \sum_n \exp\{-\beta \langle \phi_n | \hat{H} | \phi_n \rangle\}$

$\{\psi_n\}$ are complete and orthonormal. Get equality when $\{\phi_n\}$ is complete.

Equality when $\{\phi_n\}$ is complete and orthonormal is easy: $Q(\beta) = \mathrm{tr}\, e^{-\beta \hat{H}} = \mathrm{tr}(\mathbb{1}\, e^{-\beta \hat{H}}) = \mathrm{tr}(\sum_n |\phi_n\rangle\langle\phi_n| e^{-\beta \hat{H}})$

$= \sum_n \langle \phi_n | e^{-\beta \hat{H}} | \phi_n \rangle$, since $\mathbb{1} = \sum_n |\phi_n\rangle\langle\phi_n|$.

The inequality is easy if we pick ϕ_n to be eigenstates of $\hat{H}$. Then

$Q(\beta) = \sum_n \langle \phi_n | e^{-\beta \hat{H}} | \phi_n \rangle = \sum_n e^{-\beta E_n} = \sum_n e^{-\beta \langle \phi_n | \hat{H} | \phi_n \rangle}$

Each term $\langle \phi_n | e^{-\beta \hat{H}} | \phi_n \rangle = e^{-\beta E_n} \geq 0$, so if we omit some terms and don't use a complete set, we get

$$Q(\beta) > \overbrace{\sum_n{}'}^{\text{not complete}} \exp\{\beta \langle \phi_n | \hat{H} | \phi_n \rangle\}$$

what if $\{\chi_n\}$ are not eigenstates of $\hat{H}$?

Expand $\chi_n = \sum_m c_{nm} \phi_m$, where ϕ_m are a complete orthonormal set of eigenstates of $\hat{H}$, $\hat{H}|\phi_m\rangle = E_m |\phi_m\rangle$.

Unitarity says $\sum_m c_{nm}^* c_{pm} = \delta_{np}$, $\sum_n c_{nk}^* c_{nl} = \delta_{kl}$

$$Q(\beta) = \sum_n \langle \phi_n | e^{-\beta \hat{H}} | \phi_n \rangle = \sum_n \langle \chi_n | e^{-\beta \hat{H}} | \chi_n \rangle = \sum_n e^{-\beta \epsilon_n}$$

$$\sum_n \exp\{-\beta \langle \chi_n | \hat{H} | \chi_n \rangle\} = \sum_n \exp\{-\beta \sum_m |c_{nm}|^2 \langle \phi_m | \hat{H} | \phi_m \rangle\}$$

since $\langle \chi_n | \hat{H} | \chi_n \rangle = \langle \sum_m c_{nm} \phi_m | \hat{H} | \sum_p c_{np} \phi_p \rangle$

$$= \sum_{m,p} c_{nm}^* c_{np} \langle \phi_m | \hat{H} | \phi_p \rangle = \sum_m |c_{nm}|^2 \overbrace{\langle \phi_m | \hat{H} | \phi_m \rangle}^{E_m}$$

$$\langle \chi_n | e^{-\beta \hat{H}} | \chi_n \rangle = \langle \sum_m c_{nm} \phi_m | e^{-\beta \hat{H}} | \sum_p c_{np} \phi_p \rangle$$

$$= \sum_m |c_{nm}|^2 \langle \phi_m | e^{-\beta \hat{H}} | \phi_m \rangle = \sum_m |c_{nm}|^2 e^{-\beta \epsilon_m}$$

The theorem is proved if we show

$$\sum_n \sum_m |c_{nm}|^2 e^{-\beta \epsilon_m} \geq \sum_n e^{-\beta \sum_m |c_{nm}|^2 E_m}$$

Let E_m be a set of real numbers and

$\bar{E} \equiv \sum_m |c_{nm}|^2 E_m$ be a weighted avg. of these numbers E_m

with $|c_{nm}|^2 \geq 0$, $\sum_n |c_{nm}|^2 = 1$.

Let $f(E) = e^{-\beta E}$, then let

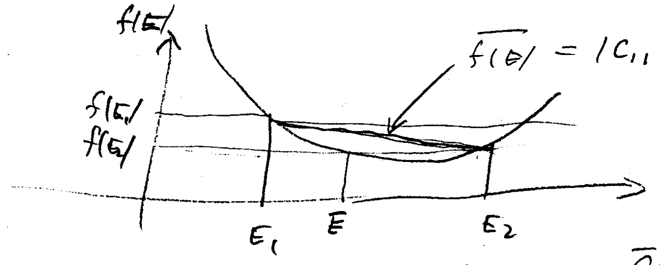
$$\overline{f(E)} = \sum_m |c_{nm}|^2 f(E_m) = \sum_m |c_{nm}|^2 e^{-\beta E_m}$$

be a weighted average of the $f(E_m)$.

Reichls' theorem requires to prove that

$$\overline{f(E)} \geq f(\bar{E}).$$

Prove this for *any* $f(E)$, not just $e^{-\beta E}$, provided $f''(E) \geq 0$, i.e. f is concave up.



$\overline{f(E)} = |C_{11}|^2 f(E_1) + |C_{12}|^2 f(E_2)$

$|C_{11}|^2 + |C_{12}|^2 = 1$

$\bar{E} = |C_{11}|^2 E_1 + |C_{12}|^2 E_2$

For 2 E_n's this is obvious. $\overline{f(E)}$ is on the line connecting $(E_1, f(E_1))$ and $(E_2, f(E_2))$, while $\bar{E}$ is on the curve connecting E_1 and E_2.

Taylor's theorem states

$$f(x) = f(x_0) + (x-x_0) f'(x_0) + \cdots + \frac{(x-x_0)^{n-1}}{(n-1)!} f^{(n-1)}(x_0) + \frac{(x-x_0)^n}{n!} f^{(n)}(x_1)$$

where for every x and x_0 there is an x_1 such that this is an equality, with $x_0 < x_1 < x$ What is x_1?

Use this for three terms,

$$f(x) = f(x_0) + (x-x_0) f'(x_0) + \frac{(x-x_0)^2}{2} f''(x_1)$$

$$\overline{f(x)} = \sum_{n=1}^{N} \lambda_n f(x_n) = \sum_{n=1}^{N} \lambda_n f(x_0) + \sum_{n=1}^{N} \lambda_n (x_n - x_0) f'(x_0) + \sum_{n=1}^{N} \lambda_n \frac{(x_n-x_0)^2}{2} f''(x_1)$$

Now let $x_0 = \sum_{n=1}^{N} \lambda_n x_n = \bar{x}$, $\lambda_n \geq 0$, $\sum \lambda_n = 1$

Then $\overline{f(x)} = f(\bar{x}) + \frac{1}{2} \overline{(x-\bar{x})^2} f''(x_1) \geq f(\bar{x})$,

since $\overline{(x-\bar{x})^2} \geq 0$ and $f''(x_1) \geq 0$.

What good is this?

$A = -kT \ln Q$, so $A \leq -kT \ln \sum_n e^{-\beta \langle \chi_n | \hat{H} | \chi_n \rangle}$

gives an upper bound to the Helmholtz free energy.

The minimum value is the exact A.

This is analogous to the variational principle for the ground state energy.