1. (a) Given the Planck Distribution $\rho(\lambda)d\lambda = \frac{8\pi hc}{\lambda^5}\frac{1}{e^{hc/\lambda kT}-1}d\lambda$

please derive Wein's displacement law: $\lambda_{\max} T = constant$ (10%)

$$c = \lambda\nu \rightarrow \nu = \frac{c}{\lambda} \Rightarrow d\nu = -\frac{c}{\lambda^2}d\lambda \quad \text{(turn into absolute value)}$$

$$\textbf{Assume } x = \frac{h\nu}{\lambda kT}, dx = \frac{-hc}{\lambda^2 kT} \quad d\lambda = \frac{-kT}{hc}x^2 d\lambda$$

$$\lambda_{\max} \quad occurs\ when\ \frac{dp(\lambda)}{d\lambda} = \frac{dp(\lambda)}{dx}\frac{dx}{d\lambda} = 0$$

$$(\frac{-kTx}{hc})^2\frac{d}{dx}\left[8\boldsymbol{\pi c}\left(\frac{-kTx}{hc}\right)^{\mathbf{5}}\frac{\mathbf{1}}{\boldsymbol{e^x - 1}}\right] = 0$$

$$(\frac{-kTx}{hc})^2 8\boldsymbol{\pi c}\left(\frac{-kTx}{hc}\right)^{\mathbf{5}}\frac{d}{dx}\left[\frac{x^5}{e^x-1}\right] = 0$$

$$\frac{d}{dx}\left[\frac{x^5}{e^x-1}\right] = 0$$

$$\frac{5e^4(e^x-1) - x^5e^x}{(e^x-1)^2} = 0$$

$$5(e^x-1) - xe^x = 5\left(1 - \frac{1}{e^x-1}\right) = 0$$

By numerical method, $\Rightarrow x \approx 5$

$$\lambda = \frac{hc}{xkT} \Rightarrow \lambda_{max}T \approx \frac{hc}{5k} = 2.9\times10^{-3}mK$$

(b) Covert the expression in (a) to frequency domain. (5%)

$$c = \lambda\nu \Rightarrow \lambda = \frac{c}{\nu} \Rightarrow \frac{d\lambda}{d\nu} = -\frac{c}{\nu^2} \Rightarrow d\lambda = -\frac{c}{\nu^2}d\nu$$

$$R(\lambda)\,d\lambda = \left(\frac{2\pi h}{\lambda^5}\right)\frac{c^2}{e^{\frac{hc}{\lambda kT}}-1}d\lambda = \left(\frac{2\pi h}{\left(\frac{c}{\nu}\right)^5}\right)\frac{c^2}{e^{\frac{h\nu}{kT}}-1}\times\frac{c}{\nu^2}d\nu$$

$$= (\frac{8\pi h\nu 3}{c^2})\frac{1}{e^{\frac{h\nu}{kT}}-1}d\nu$$

(c) What is Stefan-Boltzmann law? (5%)Please derive it from (a) or (b) (5%)

$R = \sigma T^4$

Hint: $\int_0^\infty \frac{x^3}{e^x-1}dx = \frac{\pi^4}{15}$

$$E = \int_0^\infty \frac{8\pi hc}{\lambda^5}\frac{1}{e^{hc/\lambda kt}-1}d\lambda \quad = 8\pi hc\int_0^\infty \frac{1}{\lambda^3\lambda^2}\frac{1}{e^{hc/\lambda kt}-1}d\lambda$$

let $u = \frac{hc}{\lambda kT}, \lambda = \frac{hc}{ukT}, (\lambda\rightarrow 0, u\rightarrow\infty)(\lambda\rightarrow\infty, u\rightarrow 0)$

$$\frac{du}{d\lambda}=\frac{hc}{kT},\left(\frac{-1}{\lambda^2}\right),-\frac{kT}{hc}du=\frac{d\lambda}{\lambda^2}$$

$$=8\pi hc\int_{\infty}^{0}\left(\frac{ukT}{hc}\right)^3\frac{1}{(e^u-1)}\frac{-kT}{hc}du=\frac{-8\pi k^4}{(hc)^3}T^4\int_{\infty}^{0}\frac{u^3}{(e^u-1)}du$$

$$=\frac{-8\pi k}{(hc)^3}T^4\left[\frac{-\pi^4}{15}\right]=\left(\frac{8\pi^5k^4}{15(hc)^3}\right)T^4$$

$$=\sigma T^4(\text{有寫出常數}\times T^4\text{便給分})$$

(d) Sirius, one of the hottest known stars, has approximately a blackbody spectrum with λ_{max} = 260 nm. From the Wein's displacement law $\lambda_{max}T \cong hc/5k$, find the surface temperature of Sirius. (5%)

$$\lambda_{max}T\approx\frac{hc}{5k}\rightarrow T=\frac{6.626\times10^{-34}\times2.998\times10^{17}}{260\times10^{-9}\times5\times1.381\times10^{-23}}=11064K$$

2. For the ground-state of a harmonic oscillator, $\psi_0=(\alpha/\pi)^{1/4}\,exp(-\alpha x^2/2)$, $\alpha=2\pi\nu m/\hbar$, calculate: (a) prove that ψ_0 is a solution of the Schrödinger equation with the eigenvalue 1/2 $h\nu$.(10%)

薛丁格方程式：

$$-\frac{\hbar^2}{2m}\frac{d^2\Psi(x)}{dx^2}+\frac{1}{2}kx\Psi(x)$$

$$\frac{d^2\varphi_0}{dx^2}=(\frac{\alpha}{\pi})^{\frac{1}{4}}\left[\alpha e^{\frac{-\alpha x^2}{2}}-\alpha^2x^2e^{\frac{-\alpha x^2}{2}}\right]=(-\alpha+\alpha^2x^2)\left(\frac{\alpha}{\pi}\right)^{\frac{1}{4}}e^{\frac{-\alpha x^2}{2}}$$

$$=(-\alpha+\alpha^2x^2)\varphi_0$$

$$-\frac{\hbar^2}{2m}(\alpha^2x^2-\alpha)\varphi_0+\frac{1}{2}kx^2\varphi_0=E\varphi_0$$

$$\alpha=\frac{2\pi v m}{\hbar},v=\frac{1}{2\pi}\sqrt{\frac{k}{m}}\rightarrow\alpha=\frac{\sqrt{mk}}{\hbar}$$

代入得

$$-\frac{\hbar^2}{2m}\left(\frac{mk}{\hbar^2}x^2-\frac{\sqrt{mk}}{\hbar}\right)+\frac{1}{2}kx^2=E$$

化簡得

$$E=-\frac{1}{2}kx^2+\frac{1}{2}hv+\frac{1}{2}kx^2=\frac{1}{2}hv$$

(b) For H_2 molecule, the vibrational frequency is 4403.2 cm^{-1} what is the force constant (N/m) and the vibrational zero-point energy (in kcal/mol)? (10%)

$$\tilde{\nu}=\frac{v}{c},v=\frac{1}{2\pi}\sqrt{\frac{k}{m}}$$

$$K=(443020\times C\times2\pi)^2\times\frac{1.0078^2}{2\times1.0078}\times1.66054\times10^{-27}\approx576\frac{N}{m}$$

$$E=\frac{1}{2}hv\approx4.37\times10^{-20}J\approx6.29kcal/mol$$

(c) what are the vibrational frequencies of HD and D_2? (in cm^{-1}) (H = 1.0078, D =

2.0141 amu) (10%)

$$\tilde{v}(HD) = 4403.2 \times \sqrt{\frac{\left(\frac{1.0078 \times 1.0078}{1.0078 \times 2}\right)}{\frac{(1.0078 \times 2.0141)}{(1.0078 + 2.0141)}}} \left(\sqrt{\frac{\mu H_2}{\mu HD}}\right) \approx 3814cm^{-1}$$

$$\tilde{v}(D_2) = 4403.2 \times \sqrt{\frac{\left(\frac{1.0078 \times 1.0078}{1.0078 \times 2}\right)}{\left(\frac{2.0141 \times 2.0141}{2.0141 \times 2}\right)}} \left(\sqrt{\frac{\mu H_2}{\mu D_2}}\right) \approx 3113cm^{-1}$$

(d) if $\tilde{v}x_e = 121.3\ cm^{-1}$, what is the zero-point energy and the first excited-state energy? (5%)

$E_0 = \frac{1}{2}hv - \frac{1}{4}hvx_e$

$E_v = \left(v + \frac{1}{2}\right)hv - (v+1)^2 hvx_e$, $\tilde{v} = 4403.2cm^{-1}$

$E_0 = \frac{1}{2}hc\tilde{v} - \frac{1}{4}hc(\widetilde{v}x_e) = \frac{1}{2}hc\tilde{v} - \frac{1}{4}hc(12130) = 4.3 \times 10^{-20}(J),\ 6.2kcal/mol$

$E_v = (v + \frac{1}{2})hv - (v+1)^2 hvx_e$

$= (v + \frac{1}{2})hc\tilde{v} - (v+1)^2 hc\tilde{v}x_e = 1.3 \times 10^{-19}(J),\ 18.4kcal/mol$

3. To a good approximation, the microwave spectrum of $Al^{27}H$ consists of a series of equally spaced lines, separated by 12.604 cm^{-1}. Calculate the bond distance of AlH in Å. (15%) (Al^{27} = 26.9815 amu)

For microwave spectrum (rotational spectrum)
The energy difference between two states is 2B, and for diatomic molecule

$$B = \frac{\hbar^2}{2I}, I = \mu R^2, E = hc\frac{1}{\lambda} = 2B$$

$$2B = hc(1260.4), 2 \times \frac{\hbar^2}{2I} = hc(1260.4)$$

$$I = \frac{h}{4\pi^2 c(1260.4)} = \mu R^2, \mu = \frac{1 \times 26.9815}{1 + 26.9815} \times 1.67 \times 10^{-27} \approx 1.61 \times 10^{-27}$$

$$R^2 = \frac{6.626\times10^{-34}}{4\pi^2(3\times10^8)(1260.4)(1.61\times10^{-27})} \approx 2.76 \times 10^{-20}\ ,\ R \approx 1.67Å$$

4. (a) Please justify the Dulong-Petit's law for the heat capacity of simple solids. (10%)
Dulong-Petit's law states that the molar heat capacity of solid elements is about 3R.
Dulong and Petit proposed that the specific heat of all simple (monatomic) solids is equal, approximately 25 J/mol K. The average energy of each vibration would be kT, and the total vibrational energy of one mole of atoms would be 3RT, leading to a specific heat of 3R.
(Almost all experimental results before 1872 were consistent with this law.)
(b) The Einstein heat capacity formula are:

$$C_{v,m} = 3R\, f^2$$

$$f = \frac{\theta_E}{T}\left(\frac{e^{\theta_E/2T}}{e^{\theta_E/T} - 1}\right)$$

$$\theta_E = \frac{h\nu}{k}$$

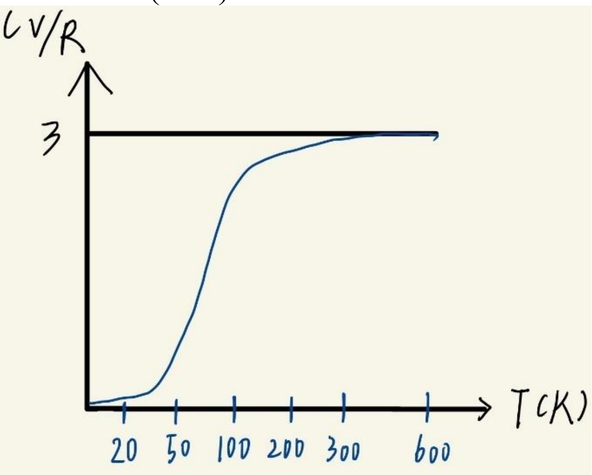
Please show the above formula gives the classical result (3R) at high temperature and zero at very low temperature. (10%)

低溫下，T 趨近於 0，因為$e^{\frac{\theta E}{T}}$很大可以忽略-1，

$f \approx \frac{\theta E}{T}\left(\frac{e^{\frac{\theta E}{2T}}}{e^{\frac{\theta E}{T}}}\right) \approx \frac{\theta E}{T} e^{\left(\frac{\theta E}{2T} - \frac{\theta E}{2T}\right)} \approx \frac{\theta E}{T} e^{\left(\frac{-\theta E}{2T}\right)}$ ，T→ $0, e^{\left(\frac{-\theta E}{2T}\right)}$下降的趨勢，比$\frac{\theta E}{T}$升高的趨勢還要快，$e^{\left(\frac{-\theta E}{2T}\right)} \to 0, f = 0$, $C_{v,m} = 0$ 所以低溫下，Cv,m=3Rf^2=3R $\times 0^2$=0

高溫下，T 趨近於∞，使用 Tayler expansion 把f展開然後取到一階項(因為越高次項，T 只會越小)，$f \approx \frac{\theta E}{T} \frac{1+\frac{\theta E}{2T}}{1+\frac{\theta E}{T}-1} \approx \frac{\theta E}{T} \frac{1+\frac{\theta E}{2T}}{\frac{\theta E}{T}} = \frac{\theta E}{T} \frac{1}{\frac{\theta E}{T}} = 1$，所以高溫下 Cv,m=3R$f^2$=3R $\times 1^2$=3R

(c) The copper metal has an approximate Einstein temperature of 300 K, plot a figure of heat capacity vs. temperature showing C_v / R at 20, 50, 100, 200, 300 and 600 K. (10%)



5. For an electron in the hydrogen 1s orbital: $\psi = \frac{1}{\sqrt{\pi}}\left(\frac{1}{a_0}\right)^{3/2} e^{-r/a_0}$

(a) Calculate the average value of r. (10 pts)

$$< r > = \int_0^{\infty} \varphi^* \hat{\gamma}\, \varphi d\tau = \int_0^{\infty} \gamma R^2{}_{nl} 4\pi r^2 dr = \int_0^{\infty} (\frac{1}{\sqrt{x}}(\frac{1}{a_0})^{\frac{3}{2}} e^{-\frac{r}{a}} 4\pi r^3 dr$$

$$= 4\left(\frac{1}{a_0}\right)^3 \int_0^{\infty} r^3 e^{-2r/a_0} dr$$

$$(\int_0^{\infty} r^n e^{-\beta r} dr = \frac{n!}{\beta^{n+1}})$$

$$< r > = 4\left(\frac{1}{a_0}\right)^3 \frac{3!}{(\frac{2}{a_0})^{3+1}} = \frac{3a_0}{2}$$

(b) Find the distance where the radial distribution function is a maximum (5 pts)

$$\text{P(r)dr} = \varphi^2 r^2 dr = \frac{1}{\pi}\left(\frac{1}{a_0}\right)^3 r^2 e^{-\frac{2r}{a_0}} dr$$

$$當 \frac{\text{P(r)}}{dr} = 0 \ 有最大值$$

$$\frac{d\left(\frac{1}{\pi}\left(\frac{1}{a_0}\right)^3 \int_0^{\infty} r^3 e^{-\frac{2r}{a_0}}\right)}{dr} = \frac{1}{\pi}\left(\frac{1}{a_0}\right)^3 \left(2re^{-\frac{2r}{a_0}} + r^2\left(\frac{-2r}{a_0}\right)e^{-\frac{2r}{a_0}}\right) = 0$$

$$\rightarrow 1 + \text{r}\left(\frac{-1}{a_0}\right) = 0, r = a_0$$

(c) Calculate the average value of the potential energy of the electron. (5 pts)

$$< v > = \int_0^{\infty} \varphi^* \hat{v}\, \varphi d\tau = \frac{1}{\pi}\left(\frac{1}{a_0}\right)^3 \int_0^{\infty} e^{-\frac{2r}{a_0}}\left(-\frac{ze^2}{4\pi\varepsilon_0 a_0}\right) r^2 4\pi dr$$

$$= -\frac{1}{\pi a_0{}^3} \frac{ze^2}{4\pi\varepsilon_0} \frac{a_0{}^2}{4} 4\pi = -\frac{ze^2}{4\pi\varepsilon_0 a_0}$$