Solutions to Pathria's Statistical Mechanics
Chapter 3

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Problem 3.1

Problem 3.2

Problem 3.3

Problem 3.4

Problem 3.5

Problem 3.6

Problem 3.7

Problem 3.11

Suppose $pV^n = C$, so the work done is

$$\Delta W = \int_{V_1}^{V_2} \frac{C}{V^n} dV = \frac{C}{n-1}(V_2^{1-n} - V_1^{1-n}) \tag{1}$$

The energy difference is given by

$$\Delta U = p_2 V_2 - p_1 V_1 = C(V_2^{1-n} - V_1^{1-n}) \tag{2}$$

Therefore, the heat absorbed is

$$\Delta Q = C\frac{n-2}{n-1}(V_2^{1-n} - V_1^{1-n}) \tag{3}$$

Problem 3.21

(a) Classically, the harmonic equation of motion leads to $x = A\sin\omega t$. As a result, the kinetic energy and potential energy will be $m\omega^2 A^2 \cos^2 \omega t/2$ and $m\omega^2 A^2 \sin^2 \omega t/2$ respectively. Average them it's easy to see that $\bar{K} = \bar{U} = m\omega^2 A^2/4$.

Quantum-mechanically, $\psi = \sum_n c_n\psi_n$ where ψ_n is the n-th Hermitian polynomial. Using the recursive relations, we have

$$\bar{K} = -\frac{\hbar^2}{2m}\sum_n |c_n|^2 \int \psi^* \frac{d^2}{dx^2}\psi dx = \sum_n |c_n|^2 \frac{\hbar\omega(2n+1)}{4} = \frac{1}{2}\sum_n |c_n|^2 E_n \tag{4}$$

$$\bar{U} = \frac{m\omega^2}{2}\sum_n |c_n|^2 \int \psi^* x^2 \psi dx = \sum_n |c_n|^2 \frac{\hbar\omega(2n+1)}{4} = \frac{1}{2}\sum_n |c_n|^2 E_n \tag{5}$$

(b) In Bohr-sommerfeld model, a quantized orbits are hypothesized, namely $m_e vr = n\hbar$. In the n-th orbit, the total energy is $E_n = -Z^2k^2e^4m_e/2\hbar^2n^2$. The radius of which is $r_n = n^2\hbar^2/Zke^2m_e$. By a naive calculation $\bar{U} = -Z^2k^2e^4m_e/\hbar^2n^2$ and $\bar{T} = Z^2k^2e^4m_e/2\hbar^2n^2$.
In the Schroedinger hydrogen atom, $\psi_{nlm} = R_{nl}(r)Y_{lm}(\theta,\phi)$. The kinetic energy is given by

$$\begin{aligned}\bar{T} &= \frac{\hbar^2}{2m}\int \psi^*_{nlm}(\frac{d^2}{dr^2} + \frac{2}{r}\frac{d}{dr} - \frac{l(l+1)}{r^2})\psi_{nlm}r^2 \sin\theta dr d\theta d\phi \\ &= \frac{\hbar^2}{2m}\int R_{nl}(r)(\frac{1}{n^2a^2})R_{nl}(r)r^2dr \\ &= \frac{e^2}{2an^2}\end{aligned} \tag{6}$$

so $\bar{U} = -e^2/an^2$. a is the Bohr radius.
(c) This is also a central force case. The results are quite identical to (b).

Problem 3.31

"Partition function" for single particle is

$$Q_1 = 1 + e^{-\varepsilon/kT}. \tag{7}$$

So a list of quatities can be obtained:

$$Q_N = (1+e^{-\varepsilon/kT})^N \tag{8}$$

$$A = -NkT\ln(1+e^{-\varepsilon/kT}) \tag{9}$$

$$\mu = -kT\ln(1+e^{-\varepsilon/kT}) \tag{10}$$

$$p = 0 \tag{11}$$

$$S = Nk\ln(1+e^{-\varepsilon/kT}) + \frac{N\varepsilon}{T}\frac{e^{-\varepsilon/kT}}{1+e^{-\varepsilon/kT}} \tag{12}$$

$$U = N\varepsilon\frac{e^{-\varepsilon/kT}}{1+e^{-\varepsilon/kT}} \tag{13}$$

$$C_p = C_V = \frac{N\varepsilon^2 e^{-\varepsilon/kT}}{kT^2(1+e^{-\varepsilon/kT})^2} \tag{14}$$

This specific heat is sometimes referred to *Schottky anomaly.*

Problem 3.41

The equilibrium temperature will be positive, since the energy of the whole system is not bounded from above. This case is a bit like the spin and lattice case. For the subsystem of spins, its energy is bounded from above, so it is possible to attain a negative temperature. While the subsystem of lattice, i.e. ideal gas in this problem, only has positive temperature. The whole system doesn't have a energy limit, so the temperature will only be positive. And energy may flow from the spin subsystem to the ideal gas.