Monatomic Ideal Gas

at room temperature and atmospheric pressure,
only atoms that form monatomic gases are noble gases
He, Ne, Ar, Kr, Xe, Ra

at ultracold temperatures,
any atom that can be trapped and cooled can form monatomic gas
including all the alkali atoms: H, Li, Na, K, Rb, Cs

degrees of freedom of single atom:

		energy scale
	position/momentum	kT
internal	electronic	$eV \sim 10^{-4} K$
	electron angular momentum	$(Z\alpha)^2 eV \sim 10^{-4} eV$
	nuclear spin	$(Z\alpha)^2 \frac{m_e}{m_p} eV \sim 10^{-7} eV$

temperature: T $\qquad \lambda_{th} = \sqrt{\frac{2\pi\hbar^2}{mkT}}$

noninteracting atoms.
nondegenerate: $\lambda_{th}^3 << V/N$

$$Z = \frac{1}{N!} Z_1^{\,N} = \frac{1}{N!}\left(\frac{V}{\lambda_{th}^3} Z_{int}\right)^N$$

internal partition function for one atom: Z_{int}

free energy: $F = -kT \log Z = F_{gas} + F_{int}$

$$F_{gas} = -NkT\left(\log \frac{V/N}{\lambda_T^3} + 1\right)$$

$$F_{int} = -NkT \log Z_{int}$$

internal contributions to the thermodynamic variables

pressure: $P_{int} = -\frac{\partial F_{int}}{\partial V} = 0$

entropy: $S_{int} = -\frac{\partial F_{int}}{\partial T} = Nk \frac{d}{dT}\left(T \log Z_{int}\right)$

chemical potential: $\mu_{int} = \frac{\partial F_{int}}{\partial N} = -kT\left(\log Z_{int}\right)$

energy $U_{int} = -\frac{\partial}{\partial \beta}\left(-\beta F_{int}\right) = NkT^2 \frac{d}{dT}\left(\log Z_{int}\right)$

heat capacity $\left(C_V\right)_{int} = \frac{\partial U_{int}}{\partial T} = Nk \frac{d}{dT}\left[T^2 \frac{d}{dT} \log Z_{int}\right]$

<u>angular-momentum degrees of freedom</u> of atom

closed shells of electrons have total spin 0, total orbital angular momentum 0
only the ν valence electrons contribute

total spin: $\vec{S} = \vec{S}_1 + \cdots + \vec{S}_\nu$
total orbital angular momentum: $\vec{L} = \vec{L}_1 + \cdots + \vec{L}_\nu$
nuclear spin: $\vec{I}$

for $Z \gtrsim 30$ and $\vec{S} \neq 0$,
most important term in internal Hamiltonian is fine-structure from spin-orbit coupling of total electron spin $\vec{S}$ and total electron orbital angular momentum $\vec{L}$

$$H_{int} = \frac{\varepsilon_{fs}}{\hbar^2} \vec{S} \cdot \vec{L}$$

$$= \frac{\varepsilon_{fs}}{2\hbar^2} \left[\vec{J}^2 - \vec{L}^2 - \vec{S}^2 \right], \text{ where } \vec{J} = \vec{L} + \vec{S}$$

eigenvalues of H_{int}:

$$\varepsilon_j = \tfrac{1}{2} \varepsilon_f \left[j(j+1) - \ell(\ell+1) - s(s+1) \right]$$

$$j = |\ell - s|, |\ell - s| + 1, \ldots, \ell + s$$

$$\text{degeneracy}: (2i+1)(2j+1)$$

internal partition function

$$Z_{int} = (2i+1) \sum_{j=|\ell-s|}^{\ell+s} (2j+1) e^{-\beta \epsilon_j}$$

high-temperature limit: $e^{-\beta \epsilon_j} \to 1$

$$Z_{int} = (2i+1)(2\ell+1)(2s+1)$$

low-temperature limit: $j = |\ell - s|$ dominates

$$Z_{int} = (2i+1)\left(2|\ell-s|+1\right) e^{-\beta \epsilon_{|\ell-s|}}$$

Ultracold Atoms

if total electron orbital angular momentum is 0,
most important term in internal Hamiltonian
is spin-spin interaction between total electron spin $\vec{S}$
and nuclear spin $\vec{I}$

$$H_{hf} = \frac{\varepsilon_{hfs}}{\hbar^2} \vec{S} \cdot \vec{I}$$

$$= \frac{\varepsilon_{hfs}}{2\hbar^2} \left[\vec{F}^2 - \vec{S}^2 - \vec{I}^2 \right] \qquad \text{hyperfine spin: } \vec{F} = \vec{I} + \vec{S}$$

angular momentum quantum numbers: s, i, f, m

$$\vec{S}^2 = s(s+1)\hbar^2$$
$$\vec{I}^2 = i(i+1)\hbar^2$$
$$\vec{F}^2 = f(f+1)\hbar^2 \qquad f = |\ell - i|, |\ell - i| + 1, \ldots, \ell + i$$
$$F_z = m\hbar \qquad m = -f, -f+1, \ldots, +f$$

eigenvalues of H_{hf}: $\varepsilon_f = \frac{1}{2}\varepsilon_{hfs}\left[f(f+1) - s(s+1) - \ell(\ell+1)\right]$

degeneracy: $2f+1$

internal partition function for

$$Z_{int} = \sum_{f=|\ell-s|}^{\ell+s} (2f+1)\, e^{-\beta\varepsilon_f}$$

high-temperature limit: $Z_{int} \to (2\ell+1)(2s+1)$
low " " : $Z_{int} \to (2|\ell-s|+1)\, e^{-\beta\varepsilon_{|\ell-s|}}$

partition function:

$$Z = \frac{1}{N!}\frac{1}{(3N)!}\left(\frac{T}{\hbar\omega}\right)^{3N} Z_{int}^{N}$$

free energy in thermodynamic limit

$$F = -kT\log Z = F_{gas} + F_{int}$$

$$F_{gas} = -3NT\left[\log\frac{T}{\hbar\omega} - \frac{4}{3}\log N + \frac{4}{3} - \sqrt{3}\right]$$

$$F_{int} = -NT\log Z_{int}$$

internal contributions to other thermodynamic variables

entropy: $S_{int} = -\frac{\partial F_{int}}{\partial T} = N\frac{d}{dT}(\log Z_{int})$

chemical potential: $\mu_{int} = +\frac{\partial F_{int}}{\partial N} = -T\log Z_{int}$

energy: $U_{int} = -\frac{\partial}{\partial\beta}(-\beta F_{int}) = +T^2\frac{d}{dT}(\log Z_{int})$