Statistics of Occupation Numbers

mean occupation number:

$$\langle n_\varepsilon \rangle = \frac{1}{z^{-1} e^{\varepsilon/kT} + a} \qquad z = e^{+\beta\mu} = e^{\mu/kT}$$

Fermi-Dirac $\Rightarrow$ $0 \leq \langle n_\varepsilon \rangle \leq 1$ $(a=1)$

Bose-Einstein $\Rightarrow$ as $\mu \to$ lowest ε $\langle n_\varepsilon \rangle \to \infty$ $(a=-1)$

$\mu < \varepsilon_0$ otherwise probabilities can be negative

- as $(\varepsilon - \mu)/kT$ becomes large $\Rightarrow$ $\langle n_\varepsilon \rangle$ for Fermi-Dirac, Bose-Einstein, and Maxwell-Boltzmann become close to each other $\Rightarrow$ quantum statistics becomes irrelevant (for Maxwell-Boltzmann

$$\langle n_\varepsilon \rangle \propto e^{-\varepsilon/kT}$$

$\exp((\varepsilon-\mu)/kT) \gg 1$ $\Rightarrow$ for all three cases $\langle n_\varepsilon \rangle \ll 1$

$\Rightarrow$ particles are essentially distinguishable

$g(\{n_\varepsilon\})$ - weight factors: $\to 1$ for Maxwell-Boltzmann

remember: ideal gas: $N = zV f(T)$

with $f(T) = \frac{(2\pi m kT)^{3/2}}{h^3}$

$$\frac{N}{V} = z f(T) \Rightarrow \frac{N}{V}\lambda^3 \ll 1$$

$$\lambda = \frac{(2\pi m kT)^{1/2}}{h}$$

de Broglie wavelength (thermal wavelength)

$\Rightarrow$ if large system is quantum,

if small system is classical

$\exp((\varepsilon-\mu)/kT) \gg 1$ $\Rightarrow$ $z \ll 1$ fugacity must be smaller than one $\Rightarrow$ $\mu < 0$

examine fluctuations in $\langle n_\varepsilon \rangle$

$$\langle n_\varepsilon^2 \rangle = \frac{1}{\tilde{Q}} \left(\left(-\frac{1}{\beta} \frac{\partial}{\partial \varepsilon} \right)^2 \tilde{Q} \right)_{z, T, \varepsilon' \neq \varepsilon}$$

$$\langle n_\varepsilon^2 \rangle - \langle n_\varepsilon \rangle^2 = \left[\left(-\frac{1}{\beta} \frac{\partial}{\partial \varepsilon} \right)^2 \ln \tilde{Q} \right]_{z, T, \varepsilon' \neq \varepsilon}$$

$$= \left[\left(-\frac{1}{\beta} \frac{\partial}{\partial \varepsilon} \right) \langle n_\varepsilon \rangle \right]_{z, T, \varepsilon' \neq \varepsilon}$$

result: $$\frac{\langle n_\varepsilon^2 \rangle - \langle n_\varepsilon \rangle^2}{\langle n_\varepsilon \rangle^2} = \left(\frac{1}{\beta} \frac{\partial}{\partial \varepsilon} \right) \left(\frac{1}{\langle n_\varepsilon \rangle} \right) = e^{\beta(\varepsilon - \mu)}$$

$$= \frac{1}{\langle n_\varepsilon \rangle} - a$$

for Maxwell - Boltzmann $a = 0 \Rightarrow$ fluctuations are "normal"

for Fermi - Dirac: $a = 1 \Rightarrow$ fluctuations become negligible as $\langle n_\varepsilon \rangle \to 1$

for Bose - Einstein: $a = -1 \Rightarrow$ fluctuations are "above normal"

according to Einstein (1909), for photons

$\frac{1}{\langle n_\varepsilon \rangle}$ - due to particle nature of light

a - due to wave nature of light

evaluate $P_\varepsilon(n)$ – probability that a particular state ε has n particles

Bose-Einstein: $$P_\varepsilon(n) = \frac{z e^{-\beta\varepsilon n}}{\left[1 - z e^{-\beta\varepsilon}\right]^{-1}} = \frac{\langle n_\varepsilon\rangle^n}{(\langle n_\varepsilon\rangle+1)^n}\,\frac{1}{\langle n_\varepsilon\rangle+1}$$

$$= \frac{\langle n_\varepsilon\rangle^n}{(\langle n_\varepsilon\rangle+1)^{n+1}}$$

(using $\langle n_\varepsilon\rangle = \dfrac{1}{z^{-1}e^{\beta\varepsilon}-1}$)

Fermi-Dirac: $$P_\varepsilon(n) = \frac{(z e^{-\beta\varepsilon})^n}{1+z e^{-\beta\varepsilon}} \quad \text{for } n = 0, 1$$

$$= \begin{cases} \langle n_\varepsilon\rangle & \text{for } n=1 \\ 1-\langle n_\varepsilon\rangle & \text{for } n=0 \end{cases}$$

Maxwell-Boltzmann: $$P_\varepsilon(n) = \frac{(z e^{-\beta\varepsilon})^n/n!}{\exp(z e^{-\beta\varepsilon})} = \frac{\langle n_\varepsilon\rangle^n}{n!}\,e^{-\langle n_\varepsilon\rangle}$$

Poisson distribution

$\dfrac{P_\varepsilon(n)}{P_\varepsilon(n-1)} \propto \dfrac{1}{n}$ for Maxwell-Boltzmann (normal for uncorrelated events)

$\dfrac{P_\varepsilon(n)}{P_\varepsilon(n-1)} = \dfrac{\langle n_\varepsilon\rangle}{\langle n_\varepsilon\rangle+1}$ → "geometric" ⇒ bosons tend to bunch together

Kinetic Considerations

$$\frac{PV}{kT} = q(z,V,T) = \frac{1}{a}\sum_{\varepsilon} \ln\left(1+az\,e^{-\beta\varepsilon}\right)$$

$$= \frac{1}{ah^3}\int d\vec{p}\,d\vec{r}\,\ln\left(1+a\,e^{-\beta(\varepsilon-\mu)}\right)$$

$$= \frac{V}{ah^3}\,4\pi\int p^2 dp\,\ln\left(1+a\,e^{-\beta(\varepsilon(p)-\mu)}\right)$$

$\Rightarrow$ pressure: $P = \frac{kT}{ah^3}\,4\pi\int p^2 dp\,\ln\left(1+a\,e^{-\beta(\varepsilon(p)-\mu)}\right)$

integrate by parts: $du = p^2 dp \quad u = \ln(1+\dots)$

$v = p^3 \quad du = \frac{a e^{-\beta(\varepsilon-\mu)}}{1+\dots}(-\beta\varepsilon')$

$$\Rightarrow P = \frac{4\pi kT}{ah^3}\Big[\underbrace{p^3\ln\left(1+a\,e^{-\beta(\varepsilon(p)-\mu)}\right)\Big|_{p=0}^{p=\infty}}_{0} + \beta\int_0^\infty \frac{a e^{-\beta(\varepsilon-\mu)}\,\varepsilon'}{1+a e^{-\beta(\varepsilon(p)-\mu)}}\,\frac{p^3}{3}\,dp\Big]$$

$$P = \frac{4\pi}{3h^3}\int_0^\infty \frac{e^{-\beta(\varepsilon-\mu)}}{1+a e^{-\beta(\varepsilon(p)-\mu)}}\,p\varepsilon'\,p^2 dp$$

since $N = \frac{4\pi V}{h^3}\int_0^\infty \frac{e^{-\beta(\varepsilon-\mu)}}{1+a e^{-\beta(\varepsilon-\mu)}}\,p^2 dp$

$\Rightarrow \quad P = \frac{1}{3}n\left\langle p\frac{d\varepsilon}{dp}\right\rangle = \frac{n}{3}\langle pu\rangle \qquad u = \frac{\partial\varepsilon}{\partial p} \Rightarrow$ velocity

for $\varepsilon = \alpha p^s \Rightarrow \frac{ns}{3}\langle \alpha p^s\rangle = \frac{ns}{3}\langle\varepsilon\rangle = \frac{s}{3}\frac{E}{V}$

main result: $P = \frac{n}{3}\left\langle p\frac{\partial\varepsilon}{\partial p}\right\rangle$ independent of particle statistics (the formula itself; the distribution over which the averaging is performed is, of course, not independent of particle statistics)

- pressure - depends on motion of particles ⇒ can it be derived from kinetic considerations alone?
- pressure arises from bombardment of container walls by particles
  - consider particles with velocities $\vec{u}$, $\vec{u}+d\vec{u}$
    ⇒ density: $f(\vec{u})$ ⇒ $\int f(\vec{u})d\vec{u}$
    ⇒ number of particles with velocities around $\vec{u}$ (in small increment $d\vec{u}$)
    $n f(\vec{u})d\vec{u}$ (per unit volume)

  - consider also a small area element on container wall $d\vec{A}$
  - question: how many will strike $d\vec{A}$ within time dt
    - all within volume $d\vec{A}\cdot\vec{u}\,dt$
    - number of such particles
      $\tilde{N} = \left((d\vec{A}\cdot\vec{u}\,dt)\, n f(\vec{u})\, d\vec{u}\right)$
    - pressure: arises from collisions at container wall ⇒ collision: momentum component of particle perpendicular to container wall reverses
      ⇒ $p_z \to -p_z$ ⇒ total momentum imparted: $2p_z$

$$P = 2n\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{0}^{\infty} 2p_z u_z n\, f(\vec{u})d\vec{u} = n\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{0}^{\infty} p_z u_z f(\vec{u})d\vec{u}$$

$$= n\langle p_z u_z\rangle = n\langle pu\cos^2\theta\rangle = \frac{n}{3}\langle pu\rangle$$

rate of effusion: rate at which particles cross a small hole on wall of container

$$R = n \int_{u_x=-\infty}^{\infty} \int_{u_y=-\infty}^{\infty} \int_{u_z=0}^{\infty} u_z \, f(\vec{u}) \, du_x \, du_y \, du_z$$

$$= n \int_0^{2\pi} \int_0^{\pi/2} \int_0^{\infty} \left(u \cos\theta \, f(\vec{u}) \right) \left(u^2 \sin\theta \, du \, d\theta \, d\phi \right)$$

$$= n \pi \int_0^{\infty} f(\vec{u}) u^3 \, du$$

$$\Rightarrow R = \frac{n \langle u \rangle}{4}$$

effused particles leave behind an anisotropic situation (only particles with momenta in direction of leaving system)

- also change energy distribution (high energy / high velocity particles leave at higher rate)

Ideal Monatomic Gas

recall: $Q(N,V,T) = \frac{[q(V,T)]^N}{N!}$

degrees of freedom: translational/electronic/nuclear

$q(V,T) = q_{trans}\, q_{elec}\, q_{nucl}$

we already know $q_{trans} = \frac{V}{\lambda^3}$ $\quad \lambda = \frac{h}{2\pi m k T}$

electronic/nuclear partition functions

- electronic partition functions ⇒ can be written as a sum over levels ⇒ $q_{elec} = \sum \omega_{ei} e^{-\beta \varepsilon_i}$

  ω_{ei} - degeneracy

  ε_i = energy

- fix $\varepsilon_0 = 0$ (ground electronic state)

  $q_{elec} = \omega_{e0} + \omega_{e1} e^{-\beta \Delta\varepsilon_{01}}$

  $\Delta\varepsilon_{01}$ - excitation energy

  typically $\Delta\varepsilon_{01}$ - order of electron volts

  $1eV = 1.1605 \times 10^4$ Kelvin

  ⇒ at typical temperatures states higher than first excited state can be neglected

  (exception: halogen atoms)

- usually one looks up tables

example: Helium: He

		deg.		energy
	$1s^2$	1	$^1S_0$	0 eV
	$1s2s$	3	$^3S_1$	19.82 eV
		1	$^1S_0$	~~20 eV~~ 20 eV

nuclear partition function

- energy levels separated by MeVs

  temperatures of 10^{10} K required to excite nuclei

- hence: usually nuclear degrees of freedom only contribute a constant shift to entropy (degeneracies)

  - condensed matter applications ⇒ neglected

$$Q = \frac{(q_{trans}\, q_{elec}\, q_{nucl})^N}{N!}$$

$$q_{trans} = \frac{V}{\lambda^3} \qquad q_{elec} = \omega_{e1} + \omega_{e2} e^{-\beta \Delta \varepsilon_{01}} + \dots$$

$$q_{nucl} = \omega_{n1}$$

- thermodynamic functions follow the usual way

$$A = -kT \ln Q = -NkT \ln q_{trans} - NkT \ln(\omega_{e1} + \omega_{e2} e^{-\beta \Delta \varepsilon_{01}}) + \dots$$

- atomic energies denoted by term symbols

  Li $1s^2\, 2s$ $\quad {}^2S_{1/2}$

  O $1s^2\, 2s^2\, 2p^4 = {}^3P_2$

  term symbol: ${}^{2S+1}L_J$

  S = quantum number characterizing total electron spin

  L = quantum number characterizing total electronic orbital angular momentum

  J = quantum number characterizing $\vec{L} + \vec{S} = \vec{J}$ (choises $|L+S|, \dots, |L-S|$)

angular momentum addition

- suppose we have $\vec{j}_1, \vec{j}_2$, two angular momenta
- in that case $\vec{j} = \vec{j}_1 + \vec{j}_2$ is also an angular momentum

$$j_x = j_{1x} + j_{2x}$$
$$j_y = j_{1y} + j_{1y}$$
$$j_z = j_{1z} + j_{2z}$$

j_x, j_y, j_z obey the angular momentum commutation relations

(what is meant by $j_{1x} + j_{2x}$? $\Rightarrow j_{1x} \otimes I_{2x} + j_{2x} \otimes I_{1y}$

tensor product, which acts on space ~~j_x~~ $|m_1\rangle \otimes |m_2\rangle$ or $|m_1 m_2\rangle$)

consider: $(j_{1z} + j_{2z})|m_1 m_2\rangle = (m_1 + m_2)|m_1 m_2\rangle$

we can have states $m_1 + m_2 = m$

m_x (maximum) can be obtained one way, if both m_1 and m_2 are maxima (m_{1x} m_{2x})

$m_x - 1$ can be obtained two ways

$m_1 = m_{1x} - 1, \; m_2 = m_{2x}$

$m_1 = m_{1x}, \; m_2 = m_{2x} - 1$

$\vdots$

overall one has

$|j_1 + j_2|, |j_1 + j_2 - 1|, \ldots, |j_1 - j_2|$

to generalize to three angular momenta $\vec{j}_1, \vec{j}_2, \vec{j}_3$

- take ~~each~~ two of the three; $\vec{j}_1, \vec{j}_2$, say

$\Rightarrow$ gives rise to $\vec{j}_{12} \Rightarrow |j_1 + j_2|, \ldots |j_1 - j_2|$

- then couple each of the $\vec{j}_{12}$ to $\vec{j}_3$

Ideal Diatomic Gas

- diatomic molecules: possess vibrational, rotational degrees of freedom, in addition to translational, electronic, and nuclear

Rigid-rotor-harmonic-oscillator approximation

Born-Oppenheimer approximation: nuclei are much more massive than electrons => move much more slowly than electrons => electrons "see" nuclei as fixed

$\Downarrow$ $\Downarrow$

as a result Schrödinger equation separates into two equations

$$H_{el}(\vec{r};\vec{R})\varphi_{el}(\vec{r};\vec{R}) = E_{el}(\vec{R})\varphi_{el}(\vec{r};\vec{R})$$

$$H_{nuc}(\vec{R})\varphi_{nuc}(\vec{R}) = E_{nuc}(\vec{R})\varphi_{nuc}(\vec{R})$$

nuclear Hamiltonian will include $E_{el}(\vec{R})$ as potential surface => nuclei move on Born-Oppenheimer potential

- solution of $H_{el}(\vec{r};\vec{R})\varphi_{el}(\vec{r};\vec{R}) = E_{el}(\vec{R})\varphi_{el}(\vec{r};\vec{R})$

  => gives potential surfaces for ground and also excited states, but usually the first excited state is eV's above ground state

  (there are exceptions!!! => for example metallic systems)

- here, we assume that diatomics interact with some potential (intramolecular), but that the intermolecular potential can be neglected
  - and further assume that the first excited state is eV's above grand state
- if we have a spherically symmetric potential

$$\left[-\frac{\hbar^2}{2m_1}\nabla_1^2 + \left(-\frac{\hbar^2}{2m_2}\vec{\nabla}_2^2\right) + V(r_{12})\right]\varphi(\vec{r}_1,\vec{r}_2) = E\varphi(\vec{r}_1,\vec{r}_2)$$

$\Downarrow$

can separate into motion of center of mass + motion of relative coordinates

$$\Rightarrow \underbrace{\left[-\frac{\hbar^2}{2M}\nabla_{\vec{R}}^2\right.}_{H_{trans}} \underbrace{\left. - \frac{\hbar^2}{2\mu}\vec{\nabla}_{\vec{r}}^2 + V(r)\right]}_{H_{rot,vib}} \varphi(\vec{r},\vec{R}) = E\varphi(\vec{r},\vec{R})$$

$M = m_1 + m_2$

$\mu = \dfrac{m_1 m_2}{m_1 + m_2}$

$\vec{r} = \vec{r}_1 - \vec{r}_2$

$\vec{R} = \dfrac{\vec{r}_1 + \vec{r}_2}{2}$

$\Downarrow$

separation of Hamiltonian into translation, internal

$$H = H_{trans} + H_{rot\text{-}vib}$$

$$q_{trans} = \left[\frac{2\pi(m_1+m_2)kT}{h^2}\right]^{3/2} V$$

$$\Rightarrow \quad q = q_{trans}\, q_{rot\text{-}vib}$$

$$Q(N,V,T) = \frac{q_{trans}^N\, q_{rot\text{-}vib}^N}{N!}$$

- relative motion consists of two types: vibration / rotation

  - expand intermuclear potential $u(r)$ about r_e (potential minimum)

$$u(r) = u(r_e) + (r-r_e)\left(\frac{du}{dr}\right)_{r=r_e} + \frac{(r-r_e)^2}{2}\left(\frac{d^2u}{dr^2}\right)_{r=r_e} + \dots$$

$$= u(r_e) + \frac{(r-r_e)^2}{2}k$$

  - for a radial harmonic oscillator we can further separate $H_{rot-vib}$ into two parts

$$H_{rot-vib} = \underbrace{H_{rot}}_{\text{angular part}} + \underbrace{H_{vib}}_{\text{radial part}}$$

  - for a two dimensional rotor (θ, φ) $\rightarrow$ $I = \mu R_0^2$

$$\varepsilon_J = \frac{\hbar^2}{2I} J(J+1) \qquad J = 0, 1, 2, \dots$$

R_0 - equilibrium bond length

  - for a simple harmonic oscillator

$$\varepsilon_n = \hbar\omega\left(n + \frac{1}{2}\right) \qquad n = 0, 1, 2, \dots$$

$$\omega = \left(\frac{k}{\mu}\right)^{1/2}$$

  - rotational spectroscopy: measures absorption lines in the microwave range: selection rule $\Delta J = \pm 1$

$$\varepsilon_{J+1} - \varepsilon_J = \frac{\hbar^2}{2I}\left[(J+1)(J+2) - J(J+1)\right]$$

$$= \frac{\hbar^2}{2I} 2(J+1)$$

lines separated by J

  - vibrational spectroscopy: measures absorption in range $\sim 1000\ cm^{-1}$ typically: selection rule $\Delta n = \pm 1$

$$\varepsilon_{n+1} - \varepsilon_n = \hbar\omega \Rightarrow \text{one line}$$

$\Rightarrow$ total Hamiltonian

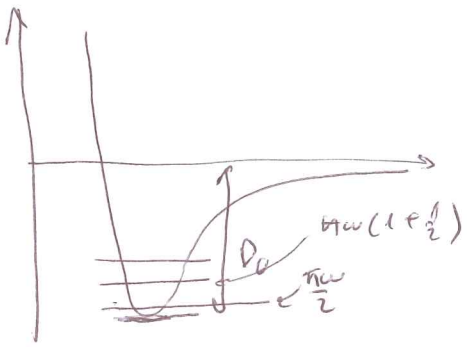
$$\mathcal{H} = \mathcal{H}_{trans} + \mathcal{H}_{rot} + \mathcal{H}_{vib} + \mathcal{H}_{elec} + \mathcal{H}_{nucl}$$

$$\Rightarrow \varepsilon = \varepsilon_{trans} + \varepsilon_{rot} + \varepsilon_{vib} + \varepsilon_{elec} + \varepsilon_{nucl}$$

$$\rightarrow q = q_{trans}\, q_{rot}\, q_{vib}\, q_{elec}\, q_{nucl}$$

$$Q(N,V,T) = \frac{(q_{trans}\, q_{rot}\, q_{vib}\, q_{nucl})^N}{N!}$$

- choosing zeroes of energies
  - for electronic subHamiltonian: choose zero to be that of neutral atoms infinitely far apart
  - for vibrational subhamiltonian: choose zero to be at the bottom of potential well



D_0 - dissociation energy

- partition functions: $q_{trans} = \frac{\lambda}{4}\frac{V}{\lambda^3}$ $\quad \lambda = \left(\frac{2\pi M kT}{h^2}\right)^{1/2}$

$$q_{elec} = \omega_{e0}\, e^{D_0/kT} + \omega_{e1}\, e^{-\varepsilon_1/kT} + \dots$$

$$q_{nucl} = \omega_S \rightarrow \text{nuclear spin degeneracy}$$

$$q_{vib} = ?$$

$$q_{rot} = ?$$

The vibrational partition function

$$\varepsilon_n = \hbar\omega\left(n+\frac{1}{2}\right)$$

$$q_{vib}(T) = \sum_n e^{-\beta\varepsilon_n} = e^{-\beta\frac{\hbar\omega}{2}}\sum_{n=0}^{\infty} e^{-\beta\hbar\omega n} = \frac{e^{-\beta\hbar\omega/2}}{1-e^{-\beta\hbar\omega}} = \frac{1}{2\sinh\left(\frac{\beta\hbar\omega}{2}\right)}$$

- can be summed explicitly; for high-T $\frac{\hbar\omega}{kT} \ll 1$

$$q_{vib}(T) = e^{-\beta\hbar\omega/2}\int_0^\infty dn\, e^{-\beta\hbar\omega n} = \frac{kT}{\hbar\omega} = \frac{T}{\Theta}$$

$\Theta = \frac{\hbar\omega}{k}$ – vibrational temperature

- average energy

$$\langle E\rangle = -\frac{\partial \ln q_{vib}(T)}{\partial\beta} = \cancel{-\frac{1}{\sum_n e^{-\beta\varepsilon_n}}\sum_n e^{-\beta\varepsilon_n}} - \frac{1}{q_{vib}(T)}\frac{\partial q_{vib}(T)}{\partial\beta}$$

$$= \cancel{\frac{(1-e^{-\beta\hbar\omega})}{e^{-}}} = +\cancel{2\sinh\left(\frac{\beta\hbar\omega}{2}\right)}\left[+\frac{1}{\cancel{2}\sinh\left(\frac{\beta\hbar\omega}{2}\right)}\right]\cosh\left(\frac{\beta\hbar\omega}{2}\right)\frac{\hbar\omega}{2}$$

$$= \coth\left(\frac{\beta\hbar\omega}{2}\right)\frac{\hbar\omega}{2} = \coth\left(\frac{\beta\hbar\omega}{2}\right)\frac{\hbar\omega}{2}$$

$$= \frac{k\Theta}{2}\coth\left(\frac{\Theta}{2T}\right) \xrightarrow{\text{for N molecules}} \frac{Nk\Theta}{2}\coth\left(\frac{\Theta}{2T}\right)$$

- specific heat:

$$C = \frac{\partial\langle E\rangle}{\partial T} = -\frac{N}{kT^2}\frac{\partial\langle E\rangle}{\partial\beta} = -\frac{\hbar\omega N}{2kT^2}\frac{\partial}{\partial\beta}\coth\left(\frac{\hbar\omega\beta}{2}\right)$$

$$= \frac{\hbar\omega N}{\cancel{2}kT^2}\left(\frac{\hbar\omega}{\cancel{2}}\right)\frac{\cancel{2}}{\sinh^2\left(\frac{\hbar\omega\beta}{2}\right)} = \frac{\hbar^2\omega^2 N}{kT^2}\frac{1}{\sinh^2\left(\frac{\hbar\omega\beta}{2}\right)}$$

$$= \frac{k\hbar^2\omega^2\beta^2 N}{\sinh^2\left(\frac{\hbar\omega}{2}\beta\right)}$$

$\beta \to 0$ (high-T limit) $\Rightarrow C \to Nk$ (equipartition verified)

$\beta \to \infty$ (low-T limit) $\Rightarrow C \to 0$