3.5 Wärmekapazität

06.06.14

Einstein-Modell

- atomarer Kristall mit N-Atomen
- jedes Atom: 3-dim-harm-OSZ.

} 3N harm-OSZ

- " " schwingt mit ν (Problematisch bei niedrigen T)

→ ÜB 5

$$C_{V,m} = \tilde{C}_V = 3R\left(\frac{\hbar\omega}{kT}\right)^2 \frac{e^{\hbar\omega/kT}}{\left(e^{\hbar\omega/kT}-1\right)^2}$$

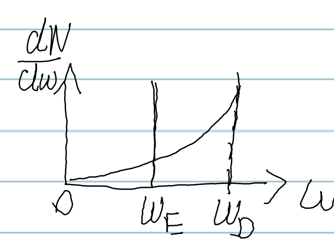
$$\hbar\omega \ll kT: \quad e^{\hbar\omega/kT} \approx 1 + \frac{\hbar\omega}{kT} + \dots$$

$$\hookrightarrow \quad \tilde{C}_V = 3R\left(\frac{\hbar\omega}{kT}\right)^2 \frac{1+\frac{\hbar\omega}{kT}}{\left(1+\frac{\hbar\omega}{kT}-1\right)^2} \approx 3R$$

(≙ Dulong-Petit-Gesetz $\approx 25\ \mathrm{J/molK}$)

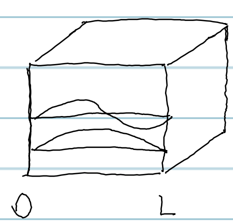
Debey-Modell

- endliche Verteilung von Frequenzen



↳ Einstein

Schwingungen im Würfel
$x = 0, L$
$y = 0, L$
$z = 0, L$



→ stehende Wellen

$$u \propto \sin(k_x x)$$

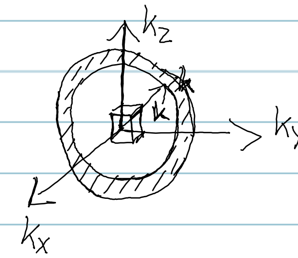
$$k_x L = n_x \pi \longrightarrow k_x = n_x \frac{\pi}{L} \quad (n_x = 0, 1, 2, \dots)$$

analoges für k_y und k_z

Schwingungen: Anzahl? $dN/d\omega$ zunächst dN/dk

↳ Wellenvektor!

$$dN = \frac{1}{8}\frac{4\pi k^2 dk}{(\pi/L)^3}\cdot 3$$



$$dN = \frac{1}{2}\frac{\pi k^2 dk}{\pi^3}\underbrace{L^3}_{V}\cdot 3 = \frac{3}{2}\frac{V}{\pi^2}k^2 dk$$

$$\left[\begin{array}{l} k = \frac{2\pi}{\lambda} = \frac{2\pi\nu}{v} = \frac{\omega}{v} \qquad \frac{d\omega}{dk} = v \longrightarrow dk = \frac{d\omega}{v} \\ \omega = k\cdot v \end{array}\right]$$

$$dN = \frac{3}{2}\frac{V}{\pi^2}\cdot\frac{\omega^2}{v^3}d\omega = \frac{3}{2}\frac{V}{\pi^2}\cdot\frac{1}{v^3}\omega^2 d\omega$$

$$\boxed{\frac{dN}{d\omega} = \frac{3}{2}\frac{V}{\pi^2}\cdot\frac{1}{v^3}\omega^2}$$

Spektrale Dichte $D(\omega)$

$$\int_0^{3N} dN = \frac{3}{2}\frac{V}{\pi^2}\cdot\frac{1}{v^3}\int_0^{\omega_D}\omega^2 d\omega$$

$$3N = \frac{\cancel{3}}{2}\frac{V}{\pi^2}\cdot\frac{1}{v^3}\cdot\frac{1}{\cancel{3}}\omega_D^3$$

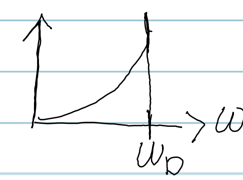
$$\omega_D^3 = 3N\frac{\pi^2 2}{V}v^3 \qquad \omega_D = \left(3N\frac{2\pi^2}{V}\right)^{1/3} v$$

Energie der Schwingungen?

$E_{ges} \longrightarrow c_V \left(\frac{\partial E_{ges}}{\partial T}\right)_V$

$$dE_{ges} = \left(n+\tfrac{1}{2}\right)\hbar\omega \, dN = \left(n+\tfrac{1}{2}\right)\hbar\omega \, D(\omega)\, d\omega$$

Debey: Frequenzen zwischen 0 und ω_D ($\hat{=}\,\omega_{max}$)



$$E_{ges} = \int_0^{\omega_D} \left(n+\tfrac{1}{2}\right)\hbar\omega\, D(\omega)\, d\omega$$

$$\tilde{c}_V = \left(\frac{\partial E_{ges}}{\partial T}\right)_V = \int_0^{\omega_D} \frac{\partial}{\partial T}\left(n+\tfrac{1}{2}\right)\hbar\omega\, D(\omega)\, d\omega \qquad n = \frac{1}{e^{\hbar\omega/kT}-1} = \left(e^{\frac{\hbar\omega}{kT}}-1\right)^{-1}$$

$$= \int_0^{\omega_D} \left(\frac{\hbar\omega}{kT^2}\right) \frac{e^{\hbar\omega/kT}}{\left(e^{\hbar\omega/kT}-1\right)^2}\, \hbar\omega\, D(\omega)\, d\omega$$

$$\tilde{c}_V = k\int_0^{\omega_D} \left(\frac{\hbar\omega}{kT}\right)^2 \frac{e^{\hbar\omega/kT}}{\left(e^{\hbar\omega/kT}-1\right)^2}\, D(\omega)\, d\omega$$

mit $x = \frac{\hbar\omega}{kT}$ und $\Theta_D = \frac{\hbar\omega_D}{k}$ Debey-Temperatur

$$\hookrightarrow \tilde{c}_V = 9R\left(T/\Theta_D\right)^3 \int_0^{\Theta_D/T} \frac{e^x}{(e^x-1)^2}\, x^4\, dx$$

$$kT \gg \hbar\omega : \quad \frac{e^x}{(e^x-1)^2} \approx \frac{1}{x^2}$$

$$\hookrightarrow \tilde{c}_V = 9R\left(T/\Theta_D\right)^3 \int_0^{\Theta_D/T} x^2\, dx = 3R \quad (\rightarrow \text{Dulong-Petit})$$

$T \to 0\,K$: $\displaystyle\int_0^\infty \frac{e^x}{(e^x-1)^2} x^4\,dx = \frac{4\pi^4}{15}$

$\hookrightarrow \boxed{\tilde{C}_V = \frac{12\pi^4}{5} R\left(T/\Theta_D\right)^3}$ Debeysches-T^3-Gesetz

gute Beschreibung experimenteller Daten mit Debey-Modell

4. Bindung und elektronische Struktur

4.1 Freies-e^--Modell

Metallische Bindung

z.B. Na

- freie und unabhängige Bewegung von e^-
- e^- spüren Potential von Ionenrümpfen (Kerne + innere e^-)

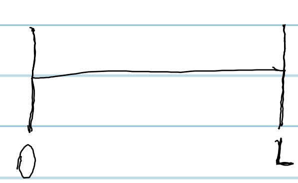
Na: $3s$-e^-

1-dim-Modell

$\hat{H}\Psi = E\Psi$

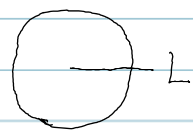
$V(x) = \text{konst.} = 0 \Rightarrow -\frac{\hbar^2}{2m}\frac{\partial^2\Psi}{\partial x^2} = E\Psi$

mögliche Modelle:



Randbed.: $\Psi(0) = \Psi(L) = 0$

stehende Wellen (Ψ)



periodische Randbed.: $\Psi(0) = \Psi(L)$
fortschreitende Wellen (Ψ)

FK $\longrightarrow$ period. Randbed.

Lösung: $\boxed{\Psi = e^{ik_x x}}$

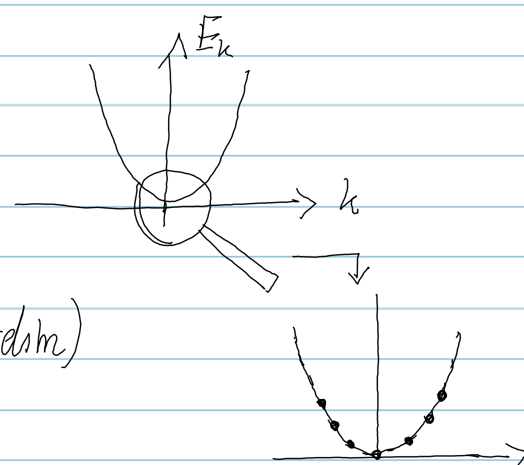
$$\Psi(0) = 1 = \Psi(L) = e^{ik_x L} \Rightarrow k_x L = n_x 2\pi \Leftrightarrow k_x = \frac{n_x 2\pi}{L}$$

$(n_x = 0; \pm 1; \pm 2; \ldots)$

3-dim-Modell

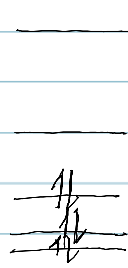
$$\Psi = \Psi(x)\,\Psi(y)\,\Psi(z)$$
$$= e^{i(k_x x + k_y y + k_z z)} = e^{i\vec{k}\vec{r}}$$

Energieeigenwerte:



$$E_k = \frac{\hbar^2}{2m} k^2 \quad (1\text{-dim})$$

$$E_k = \frac{\hbar^2}{2m}(k_x^2 + k_y^2 + k_z^2) \quad (3\text{-dim})$$



E_F 6e⁻, 0K