6.CM실패:고체열용량

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열용량

- Specific heat (heat capacity)
  - 열이 전달될 수 있는 물체의 용량
  - 열전달과정에서 온도변화가 적을수록 heat capacity는 크다

$$Q = cm\Delta T$$

Q: heat added; c: specific heat; m: mass; ΔT: change in temperature

$$C_V = \left(\frac{dQ}{dT}\right)_v = \left(\frac{dU}{dT}\right)_v \qquad C_P = \left(\frac{dQ}{dT}\right)_P = \left(\frac{dH}{dT}\right)_P \qquad \left(\frac{dH}{dT}\right)_P = \left(\frac{dU}{dT}\right)_V + R \qquad C_P = C_V + R$$

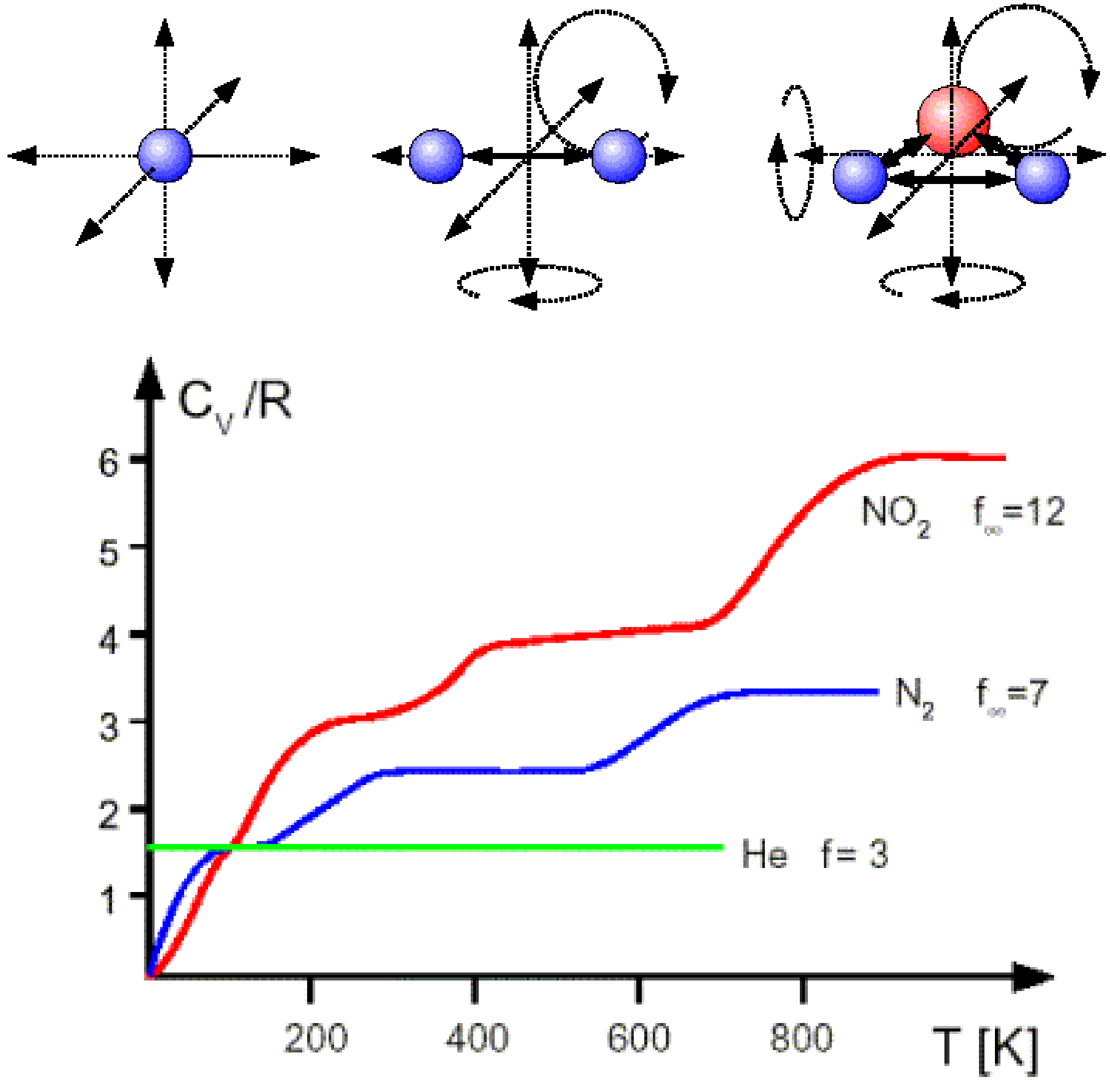
- Singular molecule

$$E_{kinetic} = E_{trans} = \frac{1}{2}mv_x^2 + \frac{1}{2}mv_y^2 + \frac{1}{2}mv_z^2 = \frac{1}{2}RT + \frac{1}{2}RT + \frac{1}{2}RT = \frac{3}{2}RT \qquad C_V = \left(\frac{dU}{dT}\right)_v = \left(\frac{dE_{trans}}{dT}\right)_v = \frac{3}{2}R = 1.5R$$

- Binary molecule

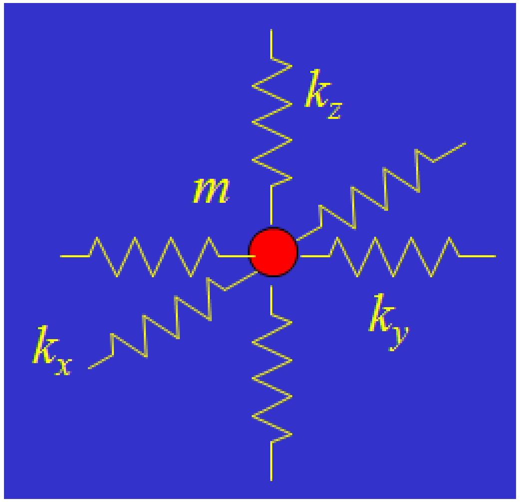
$$E_{kinetic} = E_{trans} + E_{rot} + E_{vib} = \frac{3}{2}RT + \frac{1}{2}RT + \frac{1}{2}RT = \frac{5}{2}RT \qquad C_V = \left(\frac{dU}{dT}\right)_v = \left(\frac{dE_{kinetic}}{dT}\right)_v = \frac{5}{2}R = 2.5R$$

원자수에 따른 열용량 변화



단진동 에너지

- 단진동 원자의 에너지
  - For a vibrating atom



$$E_1 = K + U$$
$$= \tfrac{1}{2}mv_x^2 + \tfrac{1}{2}mv_y^2 + \tfrac{1}{2}mv_z^2 + \tfrac{1}{2}k_x x^2 + \tfrac{1}{2}k_y y^2 + \tfrac{1}{2}k_z z^2$$

  - CM의 에너지 균등분배원리에 의해 E=1/2kT
  - 총 단진동에너지 $\overline{E}_1 = 6(\tfrac{1}{2}k_B T) = 3k_B T$

고체열용량 계산

- Dulong-Petit law
  - N개의 원자의 진동
  - 단위 몰당 에너지
  - 고체의 정적열용량
  - "300K이상의 고체 열용량은 일정하다"

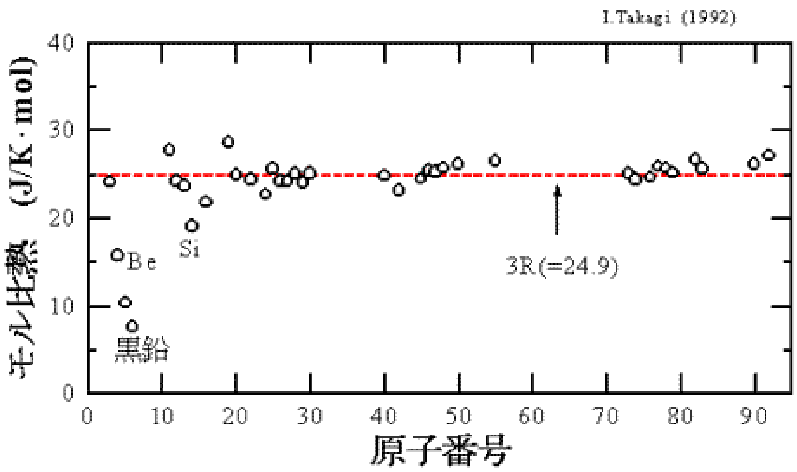
$$\bar{E} = N\bar{E}_1 = 3Nk_BT$$

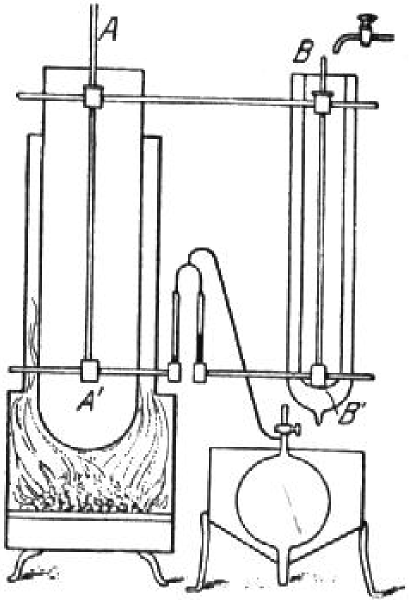
$$\frac{\bar{E}}{n} = \frac{3Nk_BT}{n} = 3N_Ak_BT = 3RT$$

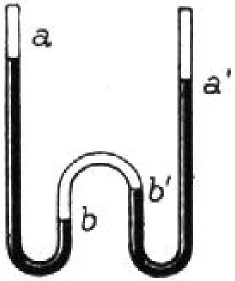
$$C_V = \frac{d}{dT}\left(\frac{\bar{E}}{n}\right)_V = 3R \approx 25\frac{J}{mol\ K}$$

Copper 0.386 J/gm °C x 63.6 gm/mole = 24.6 J/mol °C

Lead 0.128 J/gm °C x 207 gm/mole = 26.5 J/mol °C

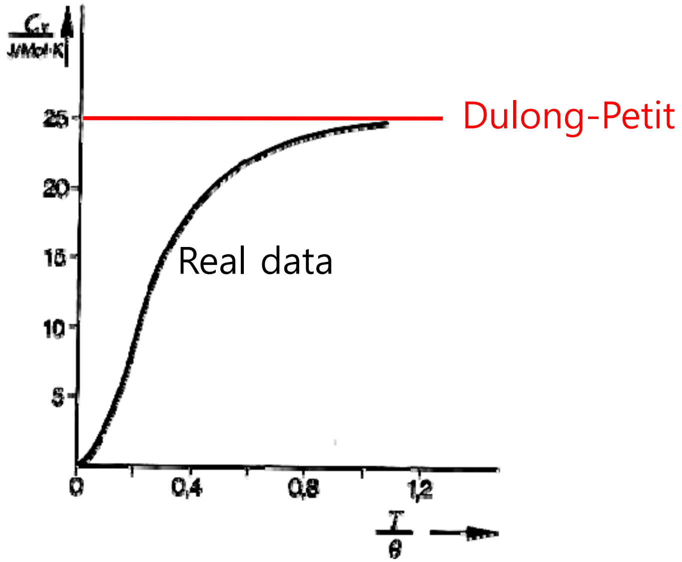


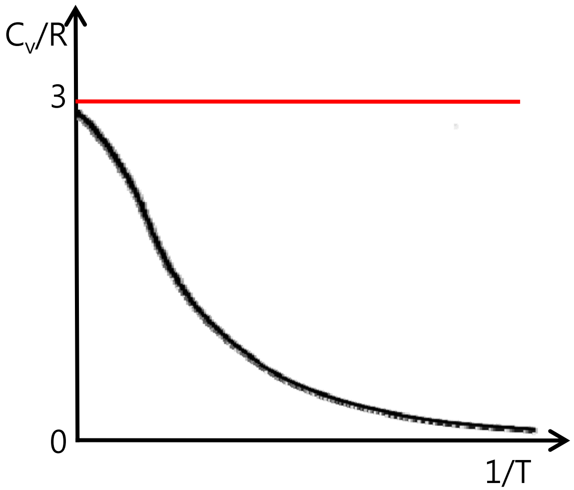




저온에서의 고체열용량

- 고온 고체열용량
  - Dulong-Petit law에 의해 3R에 근사
- 저온 고체열용량
  - 19C중반에 0K에서 C_v가 0에 근사함을 발견
  - 더 이상 D-P law가 맞지 않음

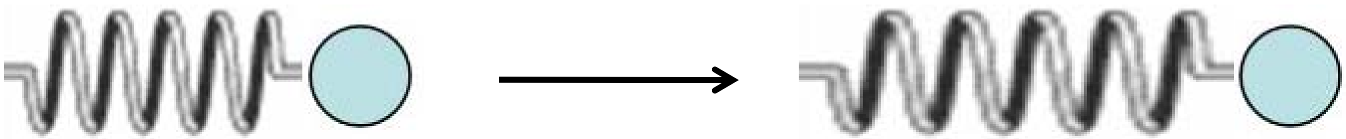




D-P law가 틀린이유

- 진동을 바라보는 CM, QM의 관점차이
  - CM: 진동은 연속적이며, 아날로그이다
    - Maxwell-Boltzmann statistics, equipartition of energy

$$E = \frac{p^2}{2m} + 2\pi^2 m \nu^2 x^2 = \frac{1}{2}mv^2 + \frac{1}{2}kx^2$$

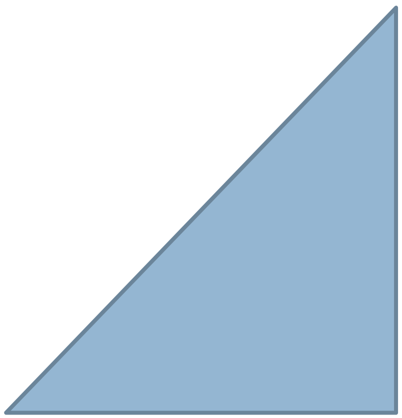


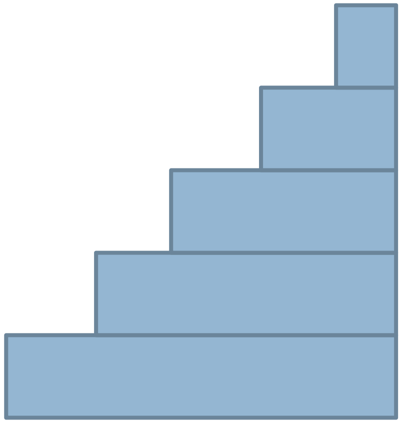
  - QM: 진동은 불연속적이며, 디지털이다
    - Quantum harmonic oscillator

$$E = nh\nu$$

해결사 아인슈타인의 등장

- 진동에너지는 QM에 의해 적분값이 아니다





$$E_{CM} = \frac{\int_0^{\infty} E e^{-\frac{E}{kT}} dE}{\int_0^{\infty} e^{-\frac{E}{kT}} dE} = kT$$

$$E_{QM} = \frac{\sum_{n=0}^{\infty} nh\nu e^{-\frac{nh\nu}{kT}}}{\sum_{n=0}^{\infty} e^{-\frac{nh\nu}{kT}}} = \frac{h\nu}{e^{h\nu/kT} - 1}$$

Einstein formula

- 아인슈타인 모델: 3방향 진동수가 모두 같다
  - 1D 단진동 vs. 3D 단진동

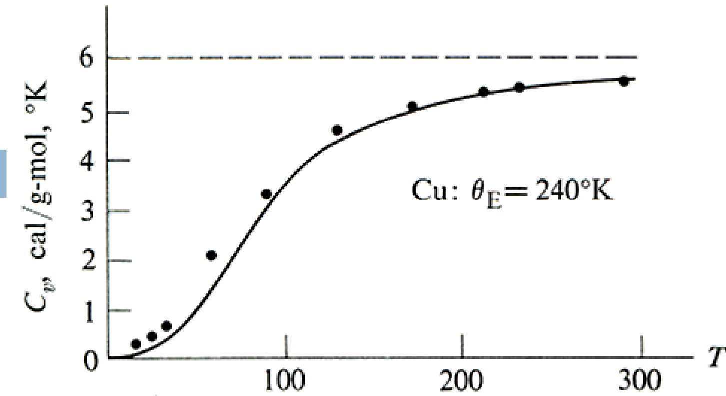
$$E = \frac{Nh\nu}{e^{h\nu/kT} - 1} \qquad E = \frac{3Nh\nu}{e^{h\nu/kT} - 1}$$

  - 고체 열용량

$$C_V = \frac{d}{dT}\left(\frac{U}{n}\right)_V = \frac{d}{dT}\left(\frac{3Nh\nu}{e^{h\nu/kT} - 1}\right) = \frac{-3Nh\nu\left[e^{h\nu/kT}\left(\frac{-h\nu}{kT^2}\right)\right]}{\left(e^{h\nu/kT} - 1\right)^2} = \frac{3R\left(\frac{h\nu}{kT}\right)^2 e^{h\nu/kT}}{\left(e^{h\nu/kT} - 1\right)^2}$$

$$C_V(T) = \frac{3R\left(\frac{\theta_E}{T}\right)^2 e^{\theta_E/T}}{\left(e^{\theta_E/T} - 1\right)^2} \qquad \theta_E \equiv \frac{h\nu}{k}$$

Einstein 식의 극한 거동



- 온도에 따른 거동

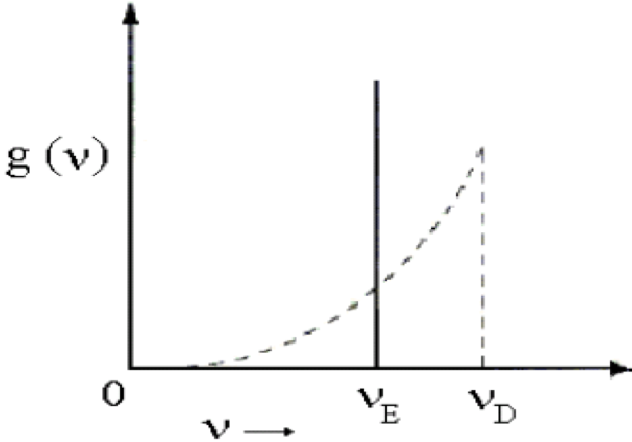
$$e^x = 1 + x + \frac{x^2}{2!} + \frac{x^3}{3!} + \frac{x^4}{4!} \ldots \qquad e^{h\nu/kT} \approx 1 + \frac{h\nu}{kT}$$

- 고온 $\frac{\theta_E}{T} << 1$ $\qquad C_V(T) \approx \frac{3R\left(\frac{\theta_E}{T}\right)^2\left(1+\frac{\theta_E}{T}\right)}{\left(1+\frac{\theta_E}{T}-1\right)^2} \approx 3R$

- 저온 $\frac{\theta_E}{T} >> 1$ $\qquad C_V(T) \approx \frac{3R\left(\frac{\theta_E}{T}\right)^2 e^{\theta_E/T}}{\left(e^{\theta_E/T}\right)^2} \approx 3R\left(\frac{\theta_E}{T}\right)^2 e^{-\theta_E/T}$

- → 실험값을 잘 맞추지만 정확하지는 않음

Debye formula



- 아인슈타인 식의 한계점 지적
  - 3방향의 진동수 동일하다는 가정은 틀리다
  - 고체내 진동모드(진동수, ν_m)의 최대값이 존재
    - 즉, 진동수는 0부터 ν_m까지 분포
  - 결정내 진동을 정상파(standing wave)로 취급
    - 원자배열간의 bond를 현과 같이 취급
  - 흑체복사의 동공내의 전자기파 mode와 유사

$$C_V(T) = \int_{\nu=0}^{\nu_m} N(\nu) C_E(\nu, T)\, d\nu$$

# of oscillators per unit ω

Einstein function for one oscillator

드바이 모델 결과

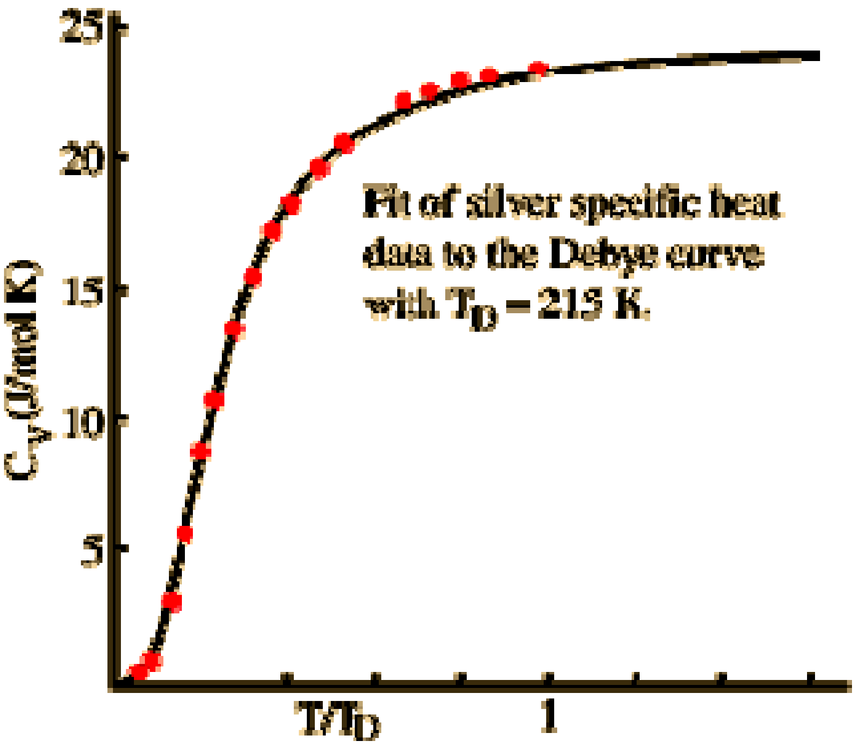
- Debye temperature
- 진동에너지

$$U = \frac{9NkT^4}{T_D^3} \int_0^{T_D/T} \frac{x^3}{e^x - 1} dx$$

- 고체열용량

$$C_V = 9Nk \left[\frac{T}{T_D}\right]^3 \int_0^{T_D/T} \frac{x^4 e^x}{(e^x - 1)^2} dx$$

$$T_D = \frac{h\upsilon_D}{k}$$



Debye 식의 극한 거동

- 고온, $T >> T_D$
  - Dulong-Petit formula와 일치

$$U = \frac{9NkT^4}{T_D^3}\int_0^{T_D/T} x^2 dx = \frac{9NkT^4}{T_D^3}\frac{T_D^3}{3T^3} = 3NkT$$

$$C_V = \frac{\partial U}{\partial T} = 3Nk$$

- 저온, $T << T_D$

$$\int_0^\infty \frac{x^3}{e^x - 1} dx = \frac{\pi^4}{15} \qquad U = \frac{3\pi^4 NkT^4}{5T_D^3} \qquad C_V = \frac{\partial U}{\partial T} = \frac{12\pi^4 Nk}{5T_D^3} T^3$$

Einstein-Debye specific heat

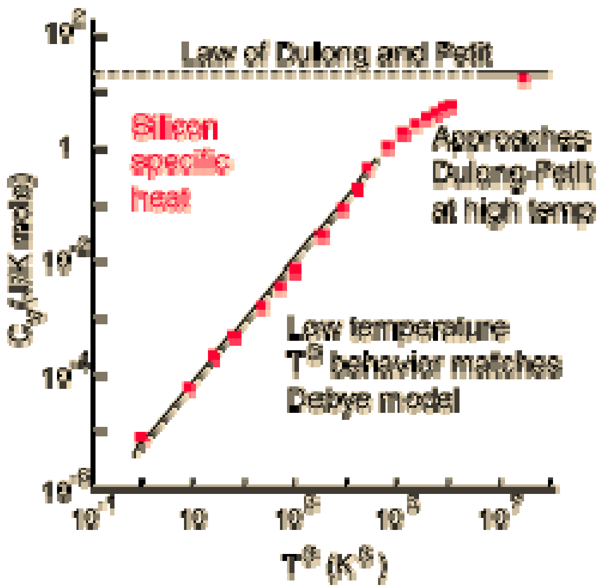
- Debye 식도 극저온에서 $C_v \sim T^3$에서 벗어남
- 보정하기 위해 electron 기여도 추가

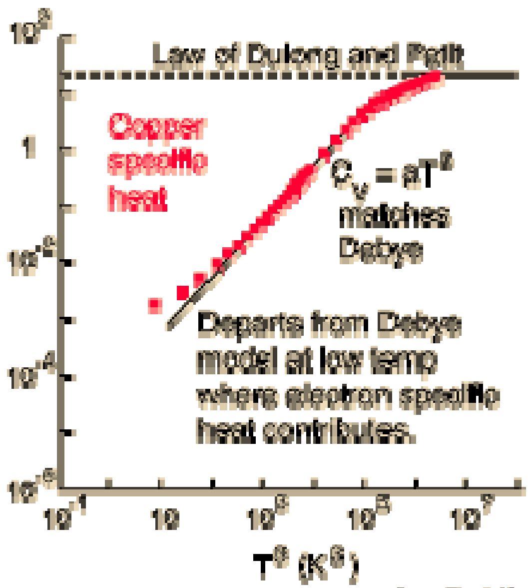
$$C = C_{electronic} + C_{vibrational}$$

$$C_{metal} = \frac{\pi^2 N_A k^2}{2E_F} T + \frac{12\pi^4 N_A k}{5T_D^3} T^3$$

Electronic specific heat proportional to temperature T

Vibrational specific heat proportional to cube of temperature T





after Rohlf