

Ch19. 熱性質

振動的熱容量

Dependence of heat capacity (at constant volume) on temperature (at low temperatures (near 0 K))

$$C_v = AT^3 \quad (19.2)$$

where A is a temperature-independent constant. Above what is called the **Debye temperature** θ_D , C_v levels off and becomes essentially independent of temperature at a value of approximately $3R$ R being the gas constant. Thus even though the total number of vibrational modes is $3N$, only a fraction of them are active at low temperatures. The thermal energy is quantized and only those modes with energy less than kT are active. The thermal energy is distributed among a series of elastic waves of various frequencies and wavelengths. The energy is quantized and only those modes with energy less than kT are active. The energy is quantized and only those modes with energy less than kT are active.

熱容量 VS 溫度

→ **Debye T³ Law** → 在低溫!!

(*材料熱的形式是 $C_v = 1943(T/\theta_D)^3$ 三方)

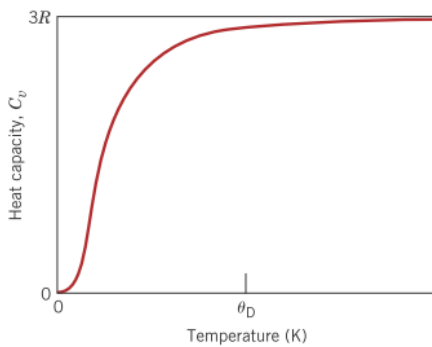


Figure 19.2 The temperature dependence of the heat capacity at constant volume; θ_D is the Debye temperature.

T 太大時就無關於溫度，差不多在 **$3R$**

其它熱容量的貢獻

EX. 電子的貢獻. 鐵磁性材料加熱超過居理溫度，電子自旋亂掉，熱容量-溫度曲線產生一個大尖點(A large spike)

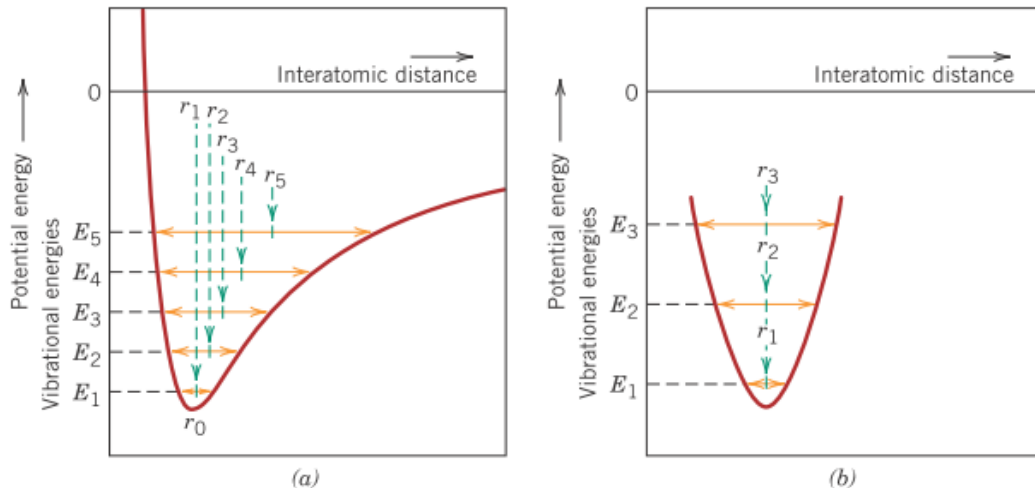
熱膨脹

$$\frac{l_f - l_0}{l_0} = \alpha_l(T_f - T_0)$$

$$\frac{\Delta l}{l_0} = \alpha_l \Delta T$$

$$\frac{\Delta V}{V_0} = \alpha_v \Delta T$$

*若等向性(isotropic)體膨脹係數為線膨脹係數的 3 倍



熱膨脹是由於位能井的非對稱性!!!而非振幅隨溫度增加

若是對稱的→無熱膨脹

越大鍵能→越深位能井→膨脹小

熱膨脹係數($\times 10^{-6}$)(度 C^{-1})

Metal→5~25

Ceramic→0.5~15 強鍵結力→低膨脹係數

* Fused silica(高純度 SiO_2 玻璃)熱膨脹係數很小:因為低原子堆積密度

Polymer→50~400 range 很廣

線性.分支----->熱固性網狀高分子 EX. phenol-formaldehyde

弱二級鍵 crosslink 增加 幾乎共價鍵

高熱膨脹係數 低熱膨脹係數

反正鍵結越強就越不會膨脹拉(深位能井)

熱傳導

$$q = -k \frac{dT}{dx}$$

類比於 Fick's 1st Law

For **steady-state heat flow**, dependence of heat flux on the thermal conductivity and the temperature gradient

機構:固體中熱的傳輸靠晶格振波(phonons)和自由電子

$$k = k_l + k_e \quad (19.6)$$

where k_l and k_e represent the lattice vibration and electron thermal conductivities,

晶格振動 (phonon)	聲子於一物體內溫度梯度存在時的淨位移(高溫→低溫) *熱能的傳遞和聲子或晶格振波運動方向一致!!
自由電子	再熱區得到動能，前一道冷區，途中與 phonon 或不純物碰撞，產生振動能，濃度越高貢獻越大(當然)B

Metal: 在純度金屬，自由電子的貢獻大於晶格振動

WHY?因為電子不像聲子較容易散射，且電子具較高速率。金屬為 good 熱導體就是為大量的自由電子參予熱傳導

自由點子→電傳導系數 VS 熱傳導系數的關係

related according to the **Wiedemann–Franz law**:

$$L = \frac{k}{\sigma T} \quad (19.7)$$

where σ is the electrical conductivity, T is the absolute temperature, and L is a constant. The theoretical value of L , $2.44 \times 10^{-8} \Omega \cdot W / (K)^2$, should be independent of temperature and the same for all metals if the heat energy is transported entirely by free electrons. Included in Table 19.1 are the experimental L values for these

雜質的影響:熱傳導和電傳導系數都會降低

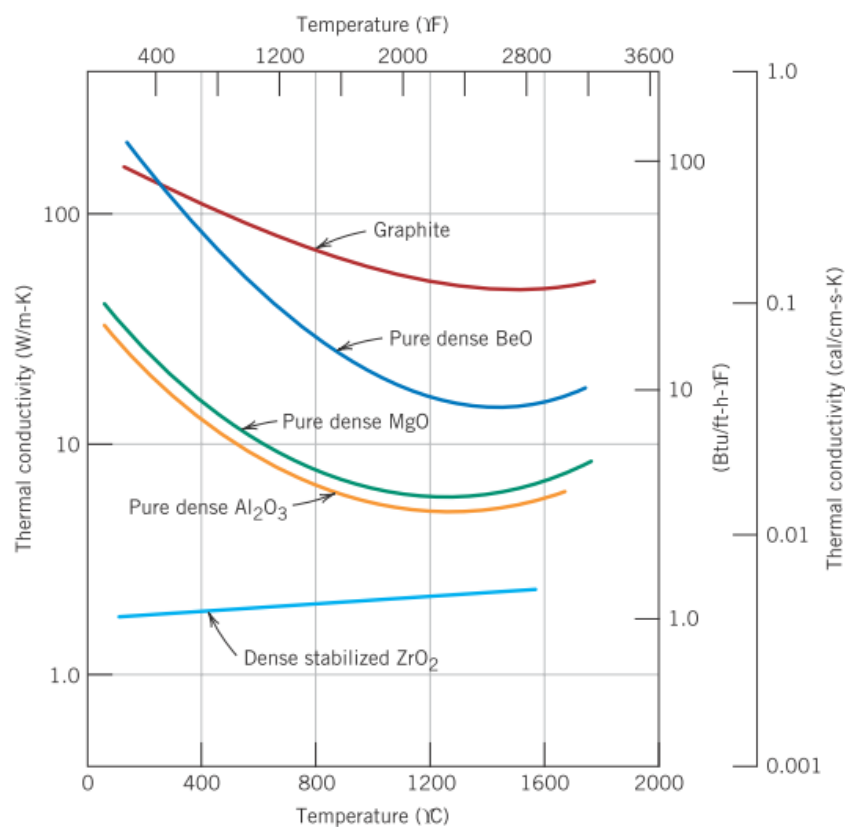
因為雜質式散射中心，降低電子運動效率!!

陶瓷→缺乏自由電子→聲子成為 main→但聲子又不像電子這麼有效(聲子容易被散射掉)

玻璃等非晶陶瓷→結構較混亂不規則→聲子散射較多→熱傳導比**結晶陶瓷**低

溫度上升→晶格振動散射增加→熱傳導降→**溫度更升**→輻射熱轉換→紅外線透過透明(**transparent**)陶瓷材料傳輸→**T 升熱傳導升**

孔隙→使熱傳導降低(後面題目有解釋題)



注意到先降
後升的曲現!
(要會解釋)

高分子:能量轉換伴隨著鏈分子的振動和旋轉，熱傳導係數大小取決於結晶度!
結晶度越高→有效分子鏈振動較多→熱傳導上升

熱應力

1. 工件有受限的熱應力

$$\sigma = E\alpha_l(T_0 - T_f) = E\alpha_l\Delta T$$

加熱時→壓

冷卻時→拉

2. 溫度梯度造成的熱應力

快速加熱 or 冷卻

3. 脆性材料的 thermal shock

延性材料及高分子，可藉由塑性變形來克服熱應力

而脆性(陶瓷)再高速冷卻時→表面為拉伸→脆不耐拉→比加熱更容易熱震

材料對於抵抗熱震的能力: thermal shock resistance parameter TSR

$$TSR \cong \frac{\sigma_f k}{E\alpha_l}$$

破裂強度.熱傳導係數高.彈性模數.熱膨脹系數低→越抗熱震

(用常理推想一下不用背~)

改善熱震: large pores or a ductile second phase

1. 加入較大孔隙
2. 延性第二相

→ impede the propagation of thermally induced crack

19.27 (a) Thermal stresses may be introduced into a structure by rapid heating or cooling because temperature gradients will be established across the cross section due to more rapid temperature changes at the surface than within the interior; thus, the surface will expand or contract at a different rate than the interior and since this surface expansion or contraction will be restrained by the interior, stresses will be introduced.

(b) For cooling, the surface stresses will be tensile in nature since the interior contracts to a lesser degree than the cooler surface.

(c) For heating, the surface stresses will be compressive in nature since the interior expands to a lesser degree than the hotter surface.

(d) For a ceramic material, thermal shock is more likely for rapid cooling since the surface stresses are tensile in nature which will lead to stress concentrations at surface flaws that are present. No such stress amplification will result for compressive stresses which are established at the surface for rapid heating.

題目

19.4 For copper, the heat capacity at constant volume C_v at 20 K is 0.38 J/mol-K, and the Debye temperature is 340 K. Estimate the specific heat **(a)** at 40 K and **(b)** at 400 K.

就代 $C_v = AT^3$ 但注意 400K 超過 Debye 溫度 $\rightarrow 3R$

19.5 The constant A in Equation 19.2 is $12\pi^4 R/5\theta_D^3$, where R is the gas constant and θ_D is the Debye temperature (K). Estimate θ_D for aluminum, given that the specific heat is 4.60 J/kg-K at 15 K.

*比熱單位要換成 J/mol-K

19.6 (a) Briefly explain why C_v rises with increasing temperature at temperatures near 0 K. **(b)** Briefly explain why C_v becomes virtually independent of temperature at temperatures far removed from 0 K.

a. 因為那時候只有一部分的 lattice waves excited，隨溫度增加，越多被 excited

b. 所有的 lattice waves 都已經 excited

19.7 A bimetallic strip is constructed from strips of two different metals that are bonded along their lengths. Explain how such a device may be used in a thermostat to regulate temperature.

熱膨脹係數不同

Q: 為啥金屬門把摸起來比塑膠方向盤冷，冬天時即使在同樣溫度

因為金屬熱傳導較高

19.15 (a) Calculate the heat flux through a sheet of brass 7.5 mm (0.30 in.) thick if the temperatures at the two faces are 150 and 50°C (302 and 122°F); assume steady-state heat flow. **(b)** What is the heat loss per hour if the area of the sheet is 0.5 m² (5.4 ft²)? **(c)** What

$$q = -k \frac{dT}{dx}$$

a. 代左式得 q (W/m²)

b. 注意 $dQ/dt = qAt$ (J/time)

*比較一下單位

19.16 (a) Would you expect Equation 19.7 to be valid for ceramic and polymeric materials? Why or why not? **(b)** Estimate the value

$$L = \frac{k}{\sigma T}$$

No, 這式子成立在自由電子對熱傳導和電傳導都有貢獻時,也就是一般金屬的狀況,而陶瓷或高分子,電子貢獻電傳導但是對熱傳導則沒啥貢獻,(陶瓷高分子熱傳導主要是靠聲子)

19.17 Briefly explain why the thermal conductivities are higher for crystalline than noncrystalline ceramics.

因為 noncrystalline,不規則的原子排序 phonon scattering 更多

*多晶→grain boundary scattering→熱傳導小於單晶

19.18 Briefly explain why metals are typically better thermal conductors than ceramic materials.

金屬→自由電子 陶瓷→聲子(易受散射)

- 19.21 (a) Porosity decreases the thermal conductivity of ceramic and polymeric materials because the thermal conductivity of a gas phase that occupies pore space is extremely small relative to that of the solid material. Furthermore, contributions from gaseous convection are generally insignificant.
- (b) Increasing the degree of crystallinity of a semicrystalline polymer enhances its thermal conductivity; the vibrations, rotations, etc. of the molecular chains are more effective modes of thermal transport when a crystalline structure prevails.

*會解釋陶瓷材料的熱傳導係數的先降後升!!