Gough-Joule 効果

エントロピーを温度と長さの二変数関数とみなす
(圧力一定)

$$dS=\left(\frac{\partial S}{\partial T}\right)_{p,L}dT+\left(\frac{\partial S}{\partial L}\right)_{T,p}dL$$

定圧熱容量 C_p

$$C_p=\left(\frac{\partial H}{\partial T}\right)_{p,L} \qquad dH=TdS+Vdp+fdL$$

$$=\left(\frac{\partial H}{\partial S}\right)_{p,L}\left(\frac{\partial S}{\partial T}\right)_{p,L}$$

$$=T\left(\frac{\partial S}{\partial T}\right)_{p,L}$$

マクスウェルの関係式

$$\left(\frac{\partial S}{\partial L}\right)_{T,p}=-\left(\frac{\partial}{\partial L}\left(\frac{\partial G}{\partial T}\right)_{p,L}\right)_{T,p}=-\left(\frac{\partial f}{\partial T}\right)_{p,L}$$

したがって

$$dS=\frac{C_p}{T}dT-\left(\frac{\partial f}{\partial T}\right)_{p,L}dL$$

ゴムに急激な変形を加えるとき、断熱変化と考える

$$q=TdS=0$$

$$\frac{C_p}{T}(dT)_s-\left(\frac{\partial f}{\partial T}\right)_{p,L}(dL)_s=0$$

$$\left(\frac{\partial T}{\partial L}\right)_{s,p}=\frac{T}{C_p}\left(\frac{\partial f}{\partial T}\right)_{p,L}$$

$\left(\frac{\partial f}{\partial T}\right)_{p,L}\neq 0$ のとき、急激な伸縮で温度変化が起こる.

体積が、λ と T に依存しないとき

$$S(R)=-\frac{\nu V k_B}{2}\left(\lambda^2+\frac{2}{\lambda}-3\right)+S_0$$

$\lambda>1$ $(L>L_0)$ の領域で

$$\left(\frac{\partial S}{\partial L}\right)_{T,p}<0 \quad , \quad \left(\frac{\partial f}{\partial T}\right)_{p,L}=-\left(\frac{\partial S}{\partial L}\right)_{T,p}>0$$ 金属と真逆

T/C_p はつねに正であるため、

$$\left(\frac{\partial T}{\partial L}\right)_{s,p}>0$$

Gough(ガー)-Joule(ジュール)効果

急激な伸長 → 温度上昇

急激な収縮 → 温度低下

実験方法

① 輪ゴムを両手で一気に引っ張る

② 伸ばしたまますぐに、鼻の下か唇に当てる → 少しあたたかい

感覚神経が集中してる

③ ゴムを一気に縮める

④ 再度、鼻の下か唇に当てる → 少し冷たい

☆ 熱弾性的反転

実際のゴムでは、$\lambda-1$ が10%程度までの領域だけ $\left(\frac{\partial f}{\partial T}\right)_{p,L}$ が負になる (エントロピーより熱膨張の影響が大きい)

x 軸方向への一軸伸長、$\lambda_x=\lambda=L/L_0$ とする

$$df=\left(\frac{\partial f}{\partial T}\right)_{p,\lambda}dT+\left(\frac{\partial f}{\partial p}\right)_{T,\lambda}dp+\left(\frac{\partial f}{\partial \lambda}\right)_{T,p}d\lambda$$

p, L 一定として、両辺を dT でわると、

$$\left(\frac{\partial f}{\partial T}\right)_{p,L}=\left(\frac{\partial f}{\partial T}\right)_{p,\lambda}+\left(\frac{\partial f}{\partial \lambda}\right)_{T,p}\left(\frac{\partial \lambda}{\partial T}\right)_{p,\lambda}$$

$$\left(\frac{\partial f}{\partial T}\right)_{p,\lambda} = \frac{\nu V_0 k_B}{L_0}\left(\lambda - \frac{1}{\lambda^2}\right) = \frac{f}{T}$$ （V_0がλに依存しないとき）

$$\left(\frac{\partial f}{\partial \lambda}\right)_{T,p} = \frac{\nu V_0 k_B T}{L_0}\left(1+\frac{2}{\lambda^3}\right) = \frac{1+2/\lambda^3}{\lambda - 1/\lambda^2} f$$

体積膨張率α_vとすると

$$\alpha_v = \frac{1}{V_0}\left(\frac{\partial V_0}{\partial T}\right)_{p,L} = \left(\frac{\partial(\ln L_0^3)}{\partial T}\right)_{p,L} = \frac{3}{L_0}\left(\frac{\partial L_0}{\partial T}\right)_{p,L}$$

$$\left(\frac{\partial \lambda}{\partial T}\right)_{p,L} = -\frac{L}{L_0^2}\left(\frac{\partial L_0}{\partial T}\right)_{p,L} = -\frac{1}{3}\frac{L}{L_0}\alpha_v = -\frac{1}{3}\lambda\alpha_v$$

$$\left(\frac{\partial f}{\partial T}\right)_{p,L} = \frac{f}{T} - \frac{1+2/\lambda^3}{3(1-1/\lambda^3)}\alpha_v f$$

熱弾性的反転が起こるのは、$(\partial f/\partial T)_{p,L}=0$のとき

$$\alpha_v T\left(1+\frac{2}{\lambda^3}\right) = 3\left(1-\frac{1}{\lambda^3}\right)$$

$$\frac{3+2\alpha_v T}{\lambda^3} = 3-\alpha_v T,$$

$$\lambda = \left(\frac{3+2\alpha_v T}{3-\alpha_v T}\right)^{\frac{1}{3}}$$

$$= \left(1+\frac{3\alpha_v T}{3-\alpha_v T}\right)^{\frac{1}{3}}$$

$$\approx 1+\frac{\alpha_v T}{3} \quad (\alpha_v T \ll 1)$$

一般的なゴム材料　$\alpha_v = 0.0005 \sim 0.001\ \mathrm{K}^{-1}$程度

$\lambda - 1 = 5\sim10\%$程度で反転

$$\left(\frac{\partial \lambda}{\partial T}\right)_{p,L} = -\frac{1}{3}\lambda\alpha_v$$

$$\lambda = \lambda_0 \exp\left(-\frac{1}{3}\alpha_v T\right)$$ 　λ_0：$T=0$のときのλ

$$\frac{1+2/\lambda^3}{3(1-1/\lambda^3)} = \frac{\lambda^3+2}{3(\lambda^3-1)}$$

$$= \frac{\lambda_0^3\exp(-\alpha_v T)+2}{3[\lambda_0^3\exp(-\alpha_v T)-1]}$$

$$\left(\frac{\partial f}{\partial T}\right)_{p,L} = \left[\frac{1}{T} - \frac{1+2/\lambda^3}{3(1-1/\lambda^3)}\alpha_v\right] f$$

$$\int\frac{1}{f}df = \int\left\{\frac{1}{T} - \frac{\lambda_0^3\exp(-\alpha_v T)+2}{3[\lambda_0^3\exp(-\alpha_v T)-1]}\alpha_v\right\}dT$$

$$\ln f = \ln T + \frac{2}{3}\alpha_v T + \ln[\lambda_0^3\exp(-\alpha_v T)-1] + C'$$

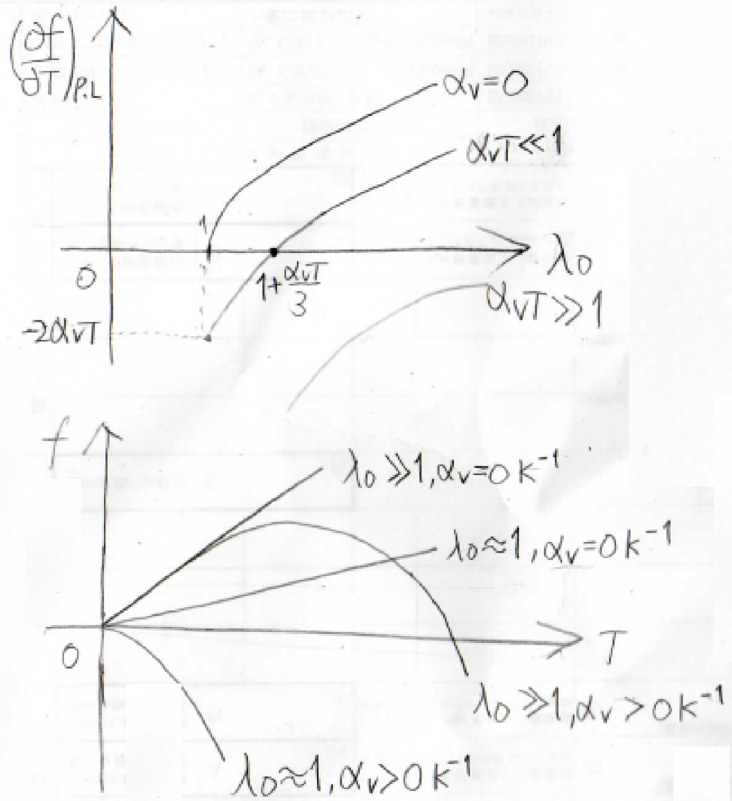
$$f = CT\left[\lambda_0^3\exp\left(-\frac{1}{3}\alpha_v T\right) - \exp\left(\frac{2}{3}\alpha_v T\right)\right]$$

$$\left(\frac{\partial f}{\partial T}\right)_{p,L} = C\left[\lambda_0^3\exp\left(-\frac{1}{3}\alpha_v T\right) - \exp\left(\frac{2}{3}\alpha_v T\right)\right]$$

$$-\frac{\alpha_v C T}{3}\left[\lambda_0^3\exp\left(-\frac{1}{3}\alpha_v T\right) + 2\exp\left(\frac{2}{3}\alpha_v T\right)\right]$$

$$= C\left[\lambda_0^3\left(1-\frac{\alpha_v T}{3}\right)\exp\left(-\frac{1}{3}\alpha_v T\right) - \left(1+\frac{2\alpha_v T}{3}\right)\exp\left(\frac{2}{3}\alpha_v T\right)\right]$$

$\alpha_v=0$のとき、$f \propto \lambda_0 - \frac{1}{\lambda_0^2}$より、$C \propto \lambda_0^2$



$\left(\frac{\partial f}{\partial T}\right)_{P,L}$
$\alpha_v=0$
$\alpha_v T \ll 1$
λ_0
0
1
$1+\frac{\alpha_v T}{3}$
$-2\alpha_v T$
$\alpha_v T \gg 1$
f
$\lambda_0 \gg 1, \alpha_v = 0\,K^{-1}$
$\lambda_0 \approx 1, \alpha_v = 0\,K^{-1}$
T
0
$\lambda_0 \gg 1, \alpha_v > 0\,K^{-1}$
$\lambda_0 \approx 1, \alpha_v > 0\,K^{-1}$