橡胶弹性

Thursday, December 10, 2020 2:49 PM

(Following Rubinstein and Colby)

补充一点热力学体系平衡态的基础

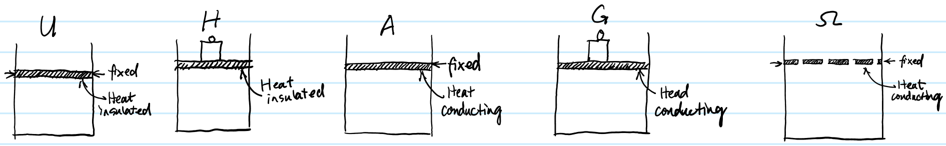
I. 橡胶拉伸的热力学：守恒律

△ 由热力学第一定律 $dE = \delta Q - \delta W$ （假设组份不变）

$\delta Q = TdS$, $\delta W = -pdV + \underbrace{fdL}_{\text{外界对系统做的功}}$

△ 把 f 视为拉伸载荷的大小，L 视为拉伸方向上的尺寸。

△ 平衡状态下，什么自由能取最小值？



△ 考虑封闭体系（没有物质交换，有能量交换），准静可逆过程，亥姆霍兹自由能

$A = E - TS$, $dA = dE - TdS - SdT = -SdT - pdV + fdL$, $A = A(T, V, L)$

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

$G = E - TS + pV$,
$dG = dE - TdS - SdT + pdV + Vdp$
$= \cancel{TdS} \cancel{-pdV} + fdL \cancel{-TdS} - SdT \cancel{+pdV} + Vdp$
$= -SdT + fdL + \underbrace{Vdp}_{=0,\ p=\text{const}}$

△ 假设 A 是足够光滑的函数，则二阶偏导数不依赖求导顺序，即：

$$\frac{\partial}{\partial L}\left(\frac{\partial}{\partial T}A\right) = \frac{\partial}{\partial T}\left(\frac{\partial}{\partial L}A\right) \Leftrightarrow -\frac{\partial S}{\partial L} = \frac{\partial f}{\partial T}$$

$-S = \frac{\partial G}{\partial T}\Big|_{p,L}$ $f = \frac{\partial G}{\partial L}\Big|_{T,p}$

$\frac{\partial}{\partial L}\left(\frac{\partial}{\partial T}G\right) = \frac{\partial}{\partial T}\left(\frac{\partial}{\partial L}G\right) \Leftrightarrow -\frac{\partial S}{\partial L}\Big|_T = \frac{\partial f}{\partial T}\Big|_L$

△ 引入了亥姆霍斯自由能之后，我们得到了 f 与 A 的关系

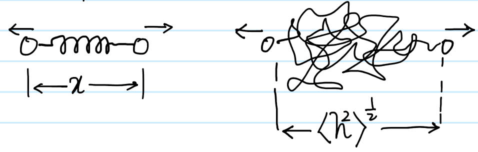
$$f = \frac{\partial A}{\partial L}\Big|_{T,V} = \frac{\partial}{\partial L}(E - TS)\Big|_{T,V} = \frac{\partial E}{\partial L}\Big|_{T,V} + T\frac{\partial S}{\partial L}\Big|_{T,V}$$

$$= \underbrace{\frac{\partial E}{\partial L}\Big|_{T,V}}_{\text{内能随伸长的变化率}} + \underbrace{T\frac{\partial f}{\partial T}\Big|_{L,V}}_{\text{保持长度不变，温度变化导致力的变化}}$$

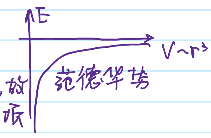
$f = \frac{\partial G}{\partial L}\Big|_{T,p} = \frac{\partial}{\partial L}(E - TS + pV)\Big|_{T,p}$

$= \frac{\partial E}{\partial L}\Big|_{T,p} + \underbrace{p\frac{\partial V}{\partial L}\Big|_{T,p}}_{\text{不可压缩},=0} - T\frac{\partial S}{\partial L}\Big|_{T,p}$

$= \frac{\partial E}{\partial L}\Big|_{T,p} + T\frac{\partial f}{\partial T}\Big|_{L,p}$



$\frac{\partial E}{\partial L}\Big|_{T,p} = \underbrace{\frac{\partial E}{\partial L}\Big|_{T,V}}_{\text{仅因链취向},\ dF_{vdw}|_V=0} + \frac{\partial E}{\partial V}\Big|_{T,L}\frac{\partial V}{\partial L}\Big|_{T,p}$，由于 $\partial E/\partial V$ 很大，故若 $\partial V/\partial L \neq 0$，整项不可忽略



$= f_E + f_S$

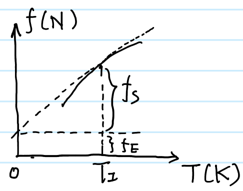
其中 $f_S = T\frac{\partial f}{\partial T}\Big|_{L,V} = \underbrace{-T\frac{\partial S}{\partial L}\Big|_{T,V}}_{\text{伸长导致的熵变(减)}}$

恒容实验是很难做的，但恒容一是直接反映微观结构贡献。恒外压过程，拉伸还会导致体系内压减小（体积膨胀）

△ f_S 的测量：测量材料在固定长度（和体积、外压下），（平衡状态的）力对温度的变化曲线，则由

$f = \frac{\partial E}{\partial L}\Big|_{T,V} + T\frac{\partial f}{\partial T}\Big|_{L,V}$,

曲线在 T_1 处的斜率是 $\frac{\partial f(T)}{\partial T}\Big|_{T=T_1}$，代入上式，



$$\frac{\partial E}{\partial L}\Big|_{T_1,V} = f_E(T_1) = f(T_1) - T_1\frac{\partial f(T)}{\partial T}\Big|_{T=T_1}$$

△ $\partial f(T)/\partial T\big|_{L,V}$，$fdL$ 的具体形式是什么？也是在求橡胶的本构方程。

II. 橡胶网络模型：本构关系

△ 我们总是可以从连续介质力学或从统计力学出发去建立一个体系的本构关系。

△ 连续介质力学出发的模型例：符合物质客观性的各向同性固体：

$\underline{\underline{\sigma}} = E\underline{\underline{B}}$， 单轴拉伸形变下即 neo-Hookian model.

Mooney-Rivlin model：单位体积的自由能（自由能密度）与应变张量$\underline{\underline{B}}$的不变量的关系：$W \equiv A/V = C_1(I_B - 3) + C_2(II_B - 3)$ | $I_B = \lambda_1^2 + \lambda_2^2 + \lambda_3^2 + 3$

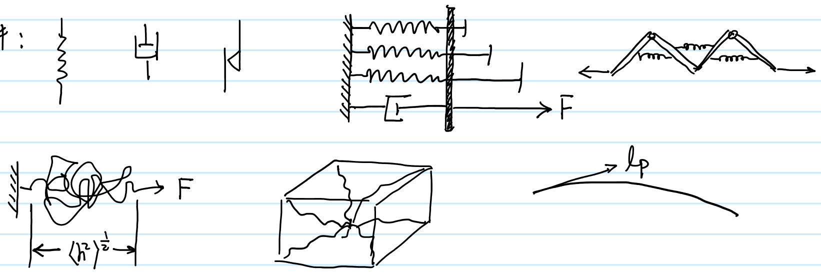
W在力学中又称strain energy. $\sigma = \frac{1}{L_x L_y}\partial A/\partial L_z = \lambda\, \partial W/\partial\lambda$ | $II_B = \lambda_1\lambda_2 + \lambda_2\lambda_3 + \lambda_1\lambda_3$

当 $C_2 = 0$ 时为neo-Hookian.

一般式：多项式超弹性模型：$W = \sum_{i,j=0}^{n} C_{ij}(I_B - 3)^i (II_B - 3)^j$

△ 微观统计模型

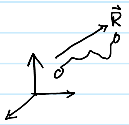
1）元件：



2）统计平均：

微观元件如何组成网络？（拓扑层面, e.g. f_c, $\overline{M}_c$, Loop/dangling/entanglements...）
宏观形变如何传递到微观元件？e.g. 仿射形变, phantom network,
自由能表达式？

例：



考虑两交联点间的一段链。
形变前：$\vec{R}_0 = (R_{x0}, R_{y0}, R_{z0})$，形变后：$\vec{R} = (\lambda_x R_{x0}, \lambda_y R_{y0}, \lambda_z R_{z0})$

由链统计，一条N个链段的链的齐三定律熵 $S(N, \vec{R}) = const - \frac{3k_B}{2Nb^2}\|\vec{R}\|^2$

仿射形变假设：$\lambda_x, \lambda_y, \lambda_z$ 就是宏观拉伸比，即

$$L_x = \lambda_x L_{x0},\quad L_y = \lambda_y L_{y0},\quad L_z = \lambda_z L_{z0}$$

假设整个网络有n条网链，每个网链都有N个链节，体系的熵等于单链熵直接求和。

$$-S_{net} = \frac{3k_B}{2Nb^2}\sum_{i=1}^{n}\|\vec{R}_i\|^2 - const = \frac{3k_B}{2Nb^2}\left(\lambda_x^2 \sum_{i=1}^{n} R_{ix_0}^2 + \lambda_y^2 \sum_{i=1}^{n} R_{iy_0}^2 + \lambda_z^2 \sum_{i=1}^{n} R_{iz_0}^2\right) - const$$

假设无形变状态下，网链取无扰尺寸即 $\langle R_{x0}^2\rangle = \langle R_{y0}^2\rangle = \langle R_{z0}^2\rangle = \frac{1}{3}Nb^2$

$$-S_{net} = -\frac{nk_B}{2}(\lambda_x^2 + \lambda_y^2 + \lambda_z^2)$$

假设不可压缩，$\lambda_x\lambda_y\lambda_z = 1$；各向同性单轴拉伸 $\lambda_x = \lambda$, $\lambda_y = \lambda_z = \lambda^{-\frac{1}{2}}$

$$f_S = -T\frac{\partial S}{\partial L_x}\Big|_T = -T\frac{\partial S}{\partial(\lambda L_{x0})}\Big|_T = -\frac{T}{L_{x0}}\frac{\partial S}{\partial\lambda}\Big|_T = \frac{nk_BT}{L_{x0}}\left(\lambda - \frac{1}{\lambda^2}\right)$$

$$\sigma_{true} \overset{def}{=} \frac{f}{L_y L_z} = \frac{f_E}{L_y L_z} + \frac{nk_BT}{L_{x0}L_y L_z}\left(\lambda - \frac{1}{\lambda^2}\right) = \frac{nk_BT}{V_0}\left(\lambda^2 - \frac{1}{\lambda}\right)$$

$$\sigma_{eng} \overset{def}{=} \frac{f}{L_{y0}L_{z0}} = \frac{\sigma_{true}}{\lambda} = \frac{nk_BT}{V_0}\left(\lambda - \frac{1}{\lambda^2}\right)$$

可见，neo-Hookean 模型等价于上述系列假设下的微观网络模型。