# An Introduction to Polymer Physics

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## Chapter 6 High-elasticity and Viscoelasticity

- 6.1 high-elasticity
- 6.2 viscoelasticity
- 6.3 linear viscoelasticity
- 6.4 superposition principles
- 6.5 dynamic viscoelasticity



## 6.1 high-elasticity

- 6.1.1 introduction
- 6.1.2 thermodynamics analysis
- 6.1.3 statistical theory
- 6.1.4 modification of equations



## 6.1.1 introduction

Mechanical property of polymer:

**High elasticity**

(small modulus, large deformation)

above Tg, caused by motion of segments

**Viscoelasticity**

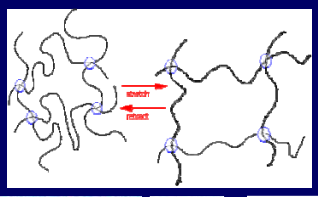
(viscosity + elasticity, time is required during deformation)

At any temperature, for all kinds of motion units

Major features



## Molecular motion: stretching and retraction




Structural requirements for high elasticity: Chain Like | Flexible | Cross-linked

High elasticity of polymer is the result that the conformational entropy changes – *the Entropy Elasticity*



## 1. Concept of high elasticity

- High elasticity – The mechanical property of polymer in rubbery state
- Rubbery state – unique, only in polymers

## High elasticity is very special

- Similar to the solids
  - Material size does not change; elastic response obeys the Hook's law, like solids;
- Similar to the liquids
  - The thermal inflation index and isothermal compression index are in the same order of magnitude of liquids;
- Similar to the gases
  - Stress increases with the temperature, similar to that the gas pressure increases with T



## 2. Features of high elasticity

A. **Large deformation**

- The strain is about 1000%, i.e. 10 times longer; for the metals, the strain is only ~1%

B. **Deformation is reversible**

**Long chains and flexibility**

origin: entropy increment; structure: crosslink



C. **Small elastic modulus, which increases with the temperature**

- E (rubber) ≈ $10^5$ N/m$^2$; E (metal) ≈ $10^{10\text{-}11}$ N/m$^2$
- E of metals goes down as temperature increases

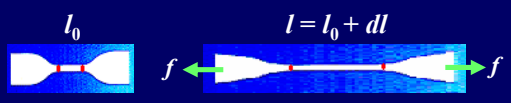
D. **Heat absorption or dissipation happens during deformation, temperature increases during fast extension**

- For the metals, it is totally different

It will be discussed in details in the following section.



## 6.1.2 thermodynamics



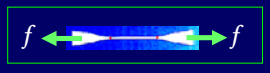

$l_0$ – Original length $dl$ – minor change of the length

$f$ – Tensile force $P$ – atm pressure $dV$ – Volume change



## First law of thermodynamics
## 热力学第一定律

$$dU = \delta Q - \delta W$$




$dU$ – Internal energy change

$\delta Q$ – heat absorbed

$\delta W$ – the work change { $PdV$ – inflation work; $Fdl$ – extension work }

$$\delta W = PdV - fdl$$

Suppose the process is reversible → 2nd law of thermodynamics → $\delta Q = TdS$



$$dU = TdS - PdV + fdl$$

The volume of the rubber does not change, that is, $dV$=0

$$dU = TdS + fdl$$

making local derivation of the length $l$

$$\left(\frac{\partial U}{\partial l}\right)_{T,V} = T\left(\frac{\partial S}{\partial l}\right)_{T,V} + f$$

$$f = \left(\frac{\partial U}{\partial l}\right)_{T,V} - T\left(\frac{\partial S}{\partial l}\right)_{T,V}$$

Internal energy change | Entropy change

Hardly measurable, shall be changed into the physical quantities detectable

## According to the Gibbs function

——吉布斯函数

*Josiah Willard Gibbs*
(1839~1903)

$G=H-TS$

*H*、*T*、*S* are the Enthalpy, Temperature and Entropy respectively

Enthalpy is a kind of thermodynamics function. It is defined as:

$H=U+PV$

*U* – internal energy;
*P* – pressure; *V* – volume



## $G=U+PV-TS$

Making derivation 求导数

$$dG=dU+PdV+VdP-TdS-SdT$$

$$dU=TdS-PdV+fdl$$

$$dG=VdP-SdT+fdl$$



## (1) 恒温恒压， i.e. *T*, *P* 不变，$dT=dP=0$

$$dG=VdP-SdT+fdl$$

$$dG=fdl,\quad f=\left(\frac{\partial G}{\partial l}\right)_{T,P}$$

## (2) 恒压恒长， i.e. *P*, *l* 不变，$dP=dl=0$

$$dG=-SdT,\quad -S=\left(\frac{\partial G}{\partial T}\right)_{P,l}$$



## Discussion

$$f=\left(\frac{\partial U}{\partial l}\right)_{T,V}-T\left(\frac{\partial S}{\partial l}\right)_{T,V}$$

$$-\left(\frac{\partial S}{\partial l}\right)_{T,V}=\left(\frac{\partial}{\partial l}\left(\frac{\partial G}{\partial T}\right)_{P,l}\right)_{T,V}=\left(\frac{\partial}{\partial T}\left(\frac{\partial G}{\partial l}\right)_{T,P}\right)_{l,V}=\left(\frac{\partial f}{\partial T}\right)_{l,V}$$

$$-S=\left(\frac{\partial G}{\partial T}\right)$$

$$f=\left(\frac{\partial G}{\partial l}\right)$$

Therefore

$$f=\left(\frac{\partial U}{\partial l}\right)_{T,V}+T\left(\frac{\partial f}{\partial T}\right)_{l,V}$$

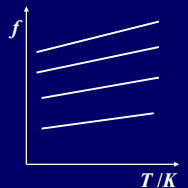
——橡胶的热力学方程



## *f* - *T* Curve

$$f=\left(\frac{\partial U}{\partial l}\right)_{T,V}+T\left(\frac{\partial f}{\partial T}\right)_{l,V}$$

- Extending the rubber to length *l* isothermally;
- measuring the force at different temperatures;
- plotting the *f* to the *T*, straight lines can be obtained. ($dV=0$)




The slop is: $\left(\frac{\partial f}{\partial T}\right)_{V,l}$

The intercept is: $\left(\frac{\partial U}{\partial l}\right)_{T,V}$

Results: when extrapolate the lines to $T=0$ *K*, *almost all the lines pass through the (0, 0)*

$$\left(\frac{\partial U}{\partial l}\right)_{T,V}\approx 0$$



## Entropy change caused by outside force

$$f=\left(\frac{\partial U}{\partial l}\right)_{T,V}-T\left(\frac{\partial S}{\partial l}\right)_{T,V}=-T\left(\frac{\partial S}{\partial l}\right)_{T,V}$$

- Conclusions:
  - Rubber elasticity is entropy elasticity
    - 橡胶弹性是熵弹性
  - Retract of rubber is caused by entropy change
    - 回弹动力是熵增

## Heat change during the extension of rubber material

$dU = 0$, $dV = 0$ $\quad dU = TdS - PdV + fdl \quad = 0$

$fdl = -TdS \qquad \delta Q = TdS$

$$-\delta Q = fdl$$

Extension $dl > 0, dS < 0, \quad \delta Q < 0$ 拉伸放热

Compression $dl < 0, dS > 0, \quad \delta Q > 0$ 回缩吸热



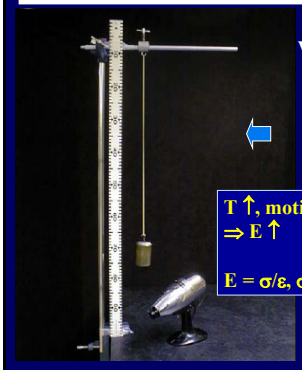
## Summary to the thermodynamics analysis

$$f = \left(\frac{\partial U}{\partial l}\right)_{T,V} - T\left(\frac{\partial S}{\partial l}\right)_{T,V}$$
$$= \left(\frac{\partial U}{\partial l}\right)_{T,V} + T\left(\frac{\partial f}{\partial T}\right)_{l,V}$$
$$= -T\left(\frac{\partial S}{\partial l}\right)_{T,V}$$

橡胶的热力学方程

- 橡胶弹性是熵弹性，回弹动力是熵增.
- 橡胶在拉伸过程中放出热量，回缩时吸收热量.





What will happen as the temperature is up?

Shrinkage of the rubber ring

T ↑, motion ↑, coil-like ↑, retract force ↑, ⇒ E ↑

$E = \sigma/\varepsilon$, $\sigma \rightarrow c$, $\varepsilon \downarrow$



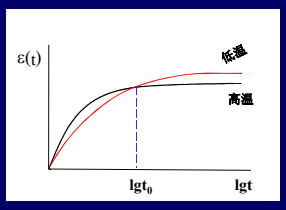
## 例题

- 按常识，温度越高，橡皮越软；而平衡高弹性的特点之一却是温度愈高，高弹平衡模量越高。这两个事实有矛盾吗？为什么？



## 例题解答

- 1) $E = 3N_0kT$, $T$升高，高分子热运动加剧，分子链趋于卷曲构象的倾向更大，回缩力更大，故高弹平衡模量越高；
- 2) 实际形变为非理想弹性形变，形变的发展需要一定松弛时间，这个松弛过程在高温时比较快，而低温时较慢，松弛时间较长，如图。按常识观察到的“温度越高，橡皮越软”就发生在非平衡态，即 $t < t_0$ 时。






## 6.1.3 statistical analysis

Statistical theory

Retraction force

Conformation change

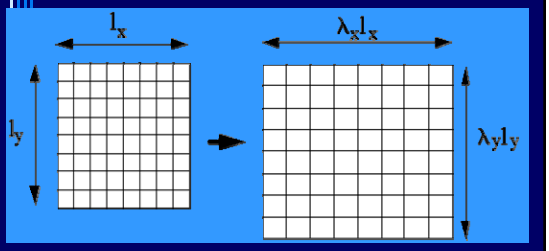
Retraction force of the material
= sum of the retraction force of all molecules

## Suppose (network)

- Before and after deformation, every joints are fixed on their equilibrium positions
- Chains between the joints are Gaussian chains
- Micro-networks are of the same deformation ratio as the whole rubber material

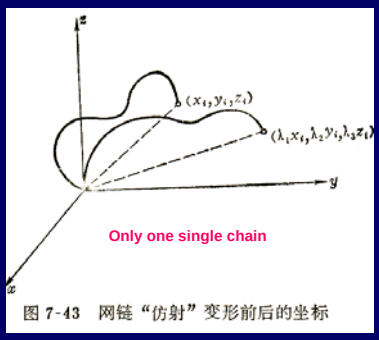


## Affine deformation仿射形变




网络中的各交联点被固定在平衡位置上，当橡胶形变时，这些交联点将以相同的比率变形。






Only one single chain

图 7-43 网链“仿射”变形前后的坐标



## Gaussian chain

For the equivalent freely jointed chains with $n_e$ segments of the length $l_e$, the probability that its free end lies in the small square $dxdydz$ (x, y, z) is:

$$W(x,y,z)dxdydz = \left(\frac{\beta}{\sqrt{\pi}}\right)^3 \exp(-\beta^2(x^2+y^2+z^2))dxdydz$$

$$\beta^2 = 3/(2n_e l_e^2)$$



Total amount of the conformation $\Omega$ is proportional to the probability W

and the entropy is $S = k\ln\Omega$

Boltzmann's law

Thus, $S = C - k\beta^2(x^2+y^2+z^2)$

C - constant



Extension ratio $\lambda_1$ $\lambda_2$ $\lambda_3$

Before extension, $(x_i, y_i, z_i)$ after, $(\lambda_1 x_i, \lambda_2 y_i, \lambda_3 z_i)$

Entropy of the $i$th chain before extension $S_i = C - k\beta_i^2(x_i^2+y_i^2+z_i^2)$

Entropy after extension $S_i' = C - k\beta_i^2(\lambda_1^2 x_i^2 + \lambda_2^2 y_i^2 + \lambda_3^2 z_i^2)$

The change of entropy $\Delta S_i = S_i' - S_i$

The entropy change of one single chain is

$$\Delta S_i = -k\beta_i^2[(\lambda_1^2-1)x_i^2+(\lambda_2^2-1)y_i^2+(\lambda_3^2-1)z_i^2]$$

The change of entropy of whole network is the addition of entropy of all single chains

$$\Delta S = -k\sum_{i=1}^{N}\beta_i^2[(\lambda_1^2-1)x_i^2+(\lambda_2^2-1)y_i^2+(\lambda_3^2-1)z_i^2]$$



Because the end-to-end distances of chains are different, the average value is used here.

$$\Delta S = -kN\beta^2[(\lambda_1^2-1)\overline{x^2}+(\lambda_2^2-1)\overline{y^2}+(\lambda_3^2-1)\overline{z^2}]$$

Number of chains $N$



For the isotropic network

$$\overline{x^2}=\overline{y^2}=\overline{z^2}=\frac{1}{3}\overline{h_0^2}$$

Mean Square end-to-end distance

$$\beta^2=\frac{3}{2n_e\overline{l_e^2}}=\frac{3}{2\overline{h_0^2}}$$

$$\Delta S = -kN\beta^2[(\lambda_1^2-1)\overline{x^2}+(\lambda_2^2-1)\overline{y^2}+(\lambda_3^2-1)\overline{z^2}]$$

$$\Delta S = -\frac{1}{2}Nk(\lambda_1^2+\lambda_2^2+\lambda_3^2-3)$$



Change of the *Helmholtz* free energy $\Delta A$

$$\Delta A = \Delta U - T\Delta S$$

$$= \frac{1}{2}NkT(\lambda_1^2+\lambda_2^2+\lambda_3^2-3)$$

For the rubbers

$\Delta U \approx 0$

During the isothermal process, the work of the outside force was stored in the system:

$$\Delta A = -\Delta W$$



Uniaxial extension 单轴拉伸

$\lambda_1=\lambda$ $\lambda_2=\lambda_3$

Incompressible materials $\lambda_1\lambda_2\lambda_3=1$

$\lambda_2=\lambda_3=1/\sqrt{\lambda}$

$$\Delta W = -\Delta A = -\frac{1}{2}NkT(\lambda_1^2+\lambda_2^2+\lambda_3^2-3)$$

$$\Delta W = -\frac{1}{2}NkT(\lambda^2+\frac{2}{\lambda}-3)$$



Extension force $f$

$-dW = fdl$ ⇒ $f=-\left(\frac{dW}{dl}\right)_{T,V}$

$\lambda = l/l_0$ ⇒ $dl = l_0 d\lambda$

$$f=-\frac{1}{l_0}\left(\frac{dW}{d\lambda}\right)_{T,V}$$

## 力-伸长比关系 *f-λ* relationship

$$f=-\frac{1}{l_0}\left(\frac{dW}{d\lambda}\right)_{T,V}$$

$$\Delta W=-\frac{1}{2}NkT\,(\lambda^2+\frac{2}{\lambda}-3)$$

$$f=-\frac{1}{l_0}\left(\frac{d[-(1/2)NkT(\lambda^2+2/\lambda-3]}{d\lambda}\right)_{T,V}$$

$$=\frac{1}{2l_0}NkT\left(\frac{d\lambda^2}{d\lambda}+2\frac{d(\lambda^{-1})}{d\lambda}\right)$$

$$=\frac{1}{2l_0}NkT\left(2\lambda-2\lambda^{-2}\right)=\frac{1}{l_0}NkT\left(\lambda-1/\lambda^2\right)$$



## σ 应力

$$\sigma=\frac{f}{A_0}=\frac{1}{A_0l_0}NkT(\lambda-\frac{1}{\lambda^2})$$

橡胶状态方程 I

$$\sigma=N_0kT(\lambda-\frac{1}{\lambda^2})$$

$N_0=N/(A_0l_0)$ – chain number in unit volume

单位体积内的网链数



Generally, the mechanical response of solid material obeys Hook's law

$$\sigma=E\varepsilon=E\frac{(l-l_0)}{l_0}=E(\lambda-1)$$

ε<<1时

由 $\lambda=1+\varepsilon$ 得,

$$\lambda^{-2}=(1+\varepsilon)^{-2}\approx1-2\varepsilon+3\varepsilon^2...$$

$$\sigma=N_0kT(\lambda-\frac{1}{\lambda^2})$$ ➡ ?



$$\lambda-\frac{1}{\lambda^2}=3\varepsilon$$

$$\sigma=3N_0kT\varepsilon$$

$$=3N_0kT(\lambda-1)$$

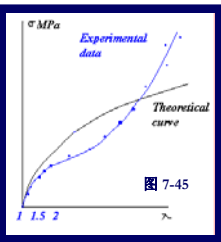


图 7-45

Conclusion: Under small strain, the σ-λ relationship is compliant to the Hook's law

结论：形变很小时，交联橡胶的应力-应变关系才符合虎克定律（见图7-45）



$$\frac{N_0}{N_A}\overline{M_c}=\rho$$ ← Avogadro's number

$\overline{M_c}$ - 交联点间链的平均分子量

$$\sigma=\frac{N_A\rho}{\overline{M_c}}kT\,(\lambda-\frac{1}{\lambda^2})=N_Ak\frac{\rho T}{\overline{M_c}}(\lambda-\frac{1}{\lambda^2})$$

$$=\frac{\rho RT}{\overline{M_c}}(\lambda-\frac{1}{\lambda^2})$$

橡胶状态方程 II



No volume change, Poisson's ratio ν is 0.5

$$E=2G(1+\nu)=3G$$

状态方程 I 改写为

$$\sigma=\frac{1}{3}E(\lambda-\frac{1}{\lambda^2})=G(\lambda-\frac{1}{\lambda^2})$$

橡胶状态方程 III

The σ-λ relationship is independent to the chemical structure of the rubbers

$E$ – original elastic modulus;

$G$ – original shear modulus

$$E = 3N_0kT \qquad G = N_0kT$$

**Modulus of the rubber increases with the temperature and the crosslinking degree**



# Summary to the equations

$$\sigma = N_0kT\left(\lambda - \frac{1}{\lambda^2}\right)$$ 橡胶状态方程1

$$\sigma = \frac{\rho RT}{\overline{M}_c}\left(\lambda - \frac{1}{\lambda^2}\right)$$ 橡胶状态方程2

$$\sigma = G\left(\lambda - \frac{1}{\lambda^2}\right)$$ 橡胶状态方程3



# 例 6-1

- 用宽度为1cm，厚度为0.2cm，长度为2.8cm的一橡皮试条，在20℃时进行拉伸试验，得到如下结果：

| 负荷（g） | 0 | 100 | 200 | 300 | 400 | 500 | 600 | 700 | 800 | 900 | 1000 |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 伸长（cm） | 0 | 0.35 | 0.7 | 1.2 | 1.8 | 2.5 | 3.2 | 4.1 | 4.9 | 5.7 | 6.5 |

- 如果橡皮试条的密度为0.964g/cm3，试计算橡皮试样网链的平均相对分子质量。



$$\because \sigma = NkT\left(\lambda - \frac{1}{\lambda^2}\right)$$

$$N = \frac{\rho}{\overline{M}_c} \cdot N_A$$

$$\therefore \sigma = \frac{\rho}{\overline{M}_c} \cdot N_A \cdot kT\left(\lambda - \frac{1}{\lambda^2}\right)$$

$$\overline{M}_c = \frac{\rho}{\sigma} \cdot N_A \cdot kT\left(\lambda - \frac{1}{\lambda^2}\right)$$

$$\overline{M}_c = \frac{\rho}{\sigma} \cdot R \cdot T\left(\lambda - \frac{1}{\lambda^2}\right)$$



已知 ρ = 0.964g/cm3，T = 293K，R = 8.314Jmol$^{-1}$K$^{-1}$

$$\sigma = F/A,\ \lambda = 1 + \varepsilon$$

| σ (g/cm²) | 500 | 1000 | 1500 | 2000 | 2500 | 3000 | 3500 | 4000 | 4500 | 5000 |
|---|---|---|---|---|---|---|---|---|---|---|
| $\lambda - \frac{1}{\lambda^2}$ | 0.80 | 1.35 | 2.00 | 2.67 | 3.42 | 4.14 | 5.06 | 5.87 | 6.7 | 7.5 |
| $\overline{M}_c \times 10^{-7}$ | 3.8 | 3.2 | 3.1 | 3.1 | 3.2 | 3.2 | 3.4 | 3.4 | 3.9 | 3.5 |

$$\overline{M}_c = 3.4 \times 10^7$$



# 例 6-2

- 一交联橡胶试片，长2.8cm，宽1.0cm，厚0.2cm，重0.518g，于25℃时将它拉伸一倍，测定张力为1.0公斤，估算试样的网链的平均相对分子质量。

由橡胶状态方程

$$M_c = \frac{\rho RT}{\sigma}\left(\lambda - \frac{1}{\lambda^2}\right)$$

$$\sigma = \frac{f}{A} = \frac{1}{0.2\times1\times10^{-4}} = 4.9\times10^5\ kg/m^2$$

$$\rho = \frac{W}{V} = \frac{0.518\times10^{-3}}{0.2\times1\times2.8\times10^{-6}} = 925 kg/m^3$$

$$\lambda = 2,\ R = 8.314 J/mol\cdot K,\ T = 298$$

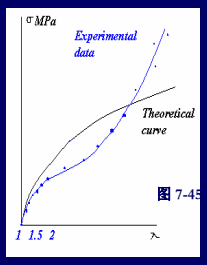
$$\overline{M}_c = \frac{925\times8.314\times298}{4.9\times10^5}\left(2 - \frac{1}{2^2}\right)$$

$$= 8180\ g/mol$$



## 6.1.4 correction to the equations

**Comparison between the experimental and theoretical data**




- Experimental data are coincide with the theoretical ones *only* when the λ value is small



## Possible reasons

- Because the chains are extended too much, they can no longer be considered as Gaussian chains
- Crystallization may happen as the chains are extended in the same direction. The E value increases.



## （1）pre-factor correction

$$\sigma = \frac{1}{2}NkT\left(\frac{\overline{h^2}}{\overline{h_0^2}}\right)\left(\lambda - \frac{1}{\lambda^2}\right)$$

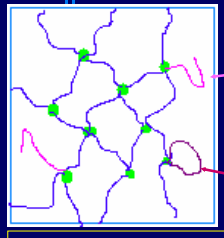
$\overline{h^2}/\overline{h_0^2}$ 前因子

令 $G_0 = \frac{1}{2}NkT\left(\frac{\overline{h^2}}{\overline{h_0^2}}\right)$ ➡ $\sigma = G_0\left(\lambda - \frac{1}{\lambda^2}\right)$



## (2) Free end correction (required)

Ideal network



Free ends

loops

$$N_0 = \frac{\rho}{\overline{M}_c}N_A$$

$$N_{end} = \frac{\rho}{\overline{M}_n}N_A$$

Number average molecular mass of original chains

Suppose there are 2 free ends for every original chains

$$N' = N_0 - 2N_{end}$$



$$N' = \frac{N_A\rho}{\overline{M}_c}\left[1 - \frac{2\overline{M}_c}{\overline{M}_n}\right]$$

Valid number of chains in unit volume, *N'*

$$\sigma = \frac{N_A kT\rho}{\overline{M}_c}\left(1 - \frac{2\overline{M}_c}{\overline{M}_n}\right)\left(\lambda - \frac{1}{\lambda^2}\right)$$

$$= \frac{\rho RT}{\overline{M}_c}\left(1 - \frac{2\overline{M}_c}{\overline{M}_n}\right)\left(\lambda - \frac{1}{\lambda^2}\right)$$

Modulus

模量

$$G = \frac{\rho RT}{\overline{M}_c}\left(1 - \frac{2\overline{M}_c}{\overline{M}_n}\right)$$

## 例 6-3

- 一块理想弹性体，其密度为 $9.5\times10^{2}kg\cdot cm^{-3}$，起始平均相对分子质量为$10^5$，交联后网链相对分子质量为$5\times10^3$，若无其它交联缺陷，只考虑链末端校正．试计算它在室温(300K)时的剪切模量。



$$G = NkT = \frac{\rho RT}{M_c}\left(1-\frac{2M_c}{M_n}\right)$$

$$= \frac{9.5\times10^2}{5\times10^3\times10^{-3}}\times8.314\times300\times\left(1-\frac{2\times5\times10^3}{10^5}\right)$$

$$= 4.75\times10^5 N\cdot m^{-2}\times\left(1-\frac{10^4}{10^5}\right)$$

$$= 4.3\times10^5 N\cdot m^{-2}$$



## 例 6-4

- 试问在室温（25 °C）下，将一截面积为0.15 $cm^2$的橡胶试样从17 cm 拉伸到21 cm需要用多大的力。（橡胶试样的密度为0.93 $g/cm^3$，交联前平均分子量为200000，交联后为6000）



$$\sigma = \frac{\rho RT}{\overline{M_c}}\left(1-\frac{2\overline{M_c}}{\overline{M_n}}\right)(\lambda-\frac{1}{\lambda^2})$$

$$= \frac{0.93\times10^6\times8.314\times298.15}{6000}\times\left(1-\frac{2\times6000}{200000}\right)\times\left(\frac{21}{17}-\frac{1}{\left(\frac{21}{17}\right)^2}\right)$$

$$= 2.09\times10^5 N/m^2$$

$$\sigma = \frac{f}{A_0} \Rightarrow f = \sigma\cdot A_0 = 2.09\times10^5\times0.15\times10^{-4} = 3.14N$$



## 例6-5

- 一橡胶试样在25 °C、应力为$1.5\times10^6 N\cdot m^{-2}$时的伸长比为2.5，试计算：
- （1）每立方厘米中的网络链数目，假定橡胶为理想网络；
- （2）在25°C 伸长比为1.5 时所需要的应力；
- （3）在100°C 伸长比为2.5 时所需的应力。



**解:** $\sigma = N_0 kT\left(\lambda-\frac{1}{\lambda^2}\right)$

（1） $N_0 = \frac{\sigma}{kT\left(\lambda-\frac{1}{\lambda^2}\right)} = \frac{1.5\times10^6}{1.38\times10^{-23}\times298.15\times\left(2.5-\frac{1}{2.5^2}\right)} = 1.558\times10^{26}/m^3$

（2） $\sigma = N_0 kT\left(\lambda-\frac{1}{\lambda^2}\right) = 1.558\times10^{26}\times1.38\times10^{-23}\times298.15\times\left(1.5-\frac{1}{1.5^2}\right)$

$= 6.76\times10^5 N/m^2$

（3） $\sigma = N_0 kT\left(\lambda-\frac{1}{\lambda^2}\right) = 1.558\times10^{26}\times1.38\times10^{-23}\times373.15\times\left(2.5-\frac{1}{2.5^2}\right)$

$= 1.88\times10^6 N/m^2$

## 6.2 Viscoelasticity

### 6.2.1 introduction

Normal concept of **viscosity** and **elasticity**

**elasticity** – spring, ejection, deformation reversible

**Viscosity** – glue, sticky, deformation not reversible



## viscosity & elasticity of materials

Different response to the outside force of the material

- Constant force or deformation – **static VE**
- Variable force or deformation – **dynamic VE**

**Typically** Solid of small molecules - elastic

liquid of small molecules - viscous

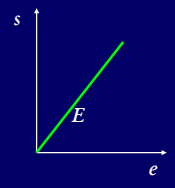


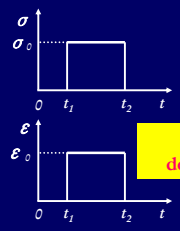
## Hook's law

*Ideal elastic solid*

$$\sigma = E\varepsilon$$

*弹性模量 Elastic modulus*




No time dependence

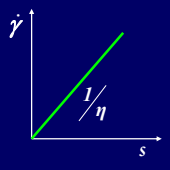


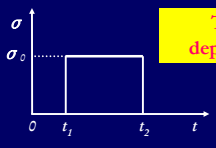
## Newtonian law

*Ideal viscous liquid*

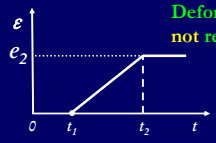
$$\sigma = \eta\dot{\gamma} = \eta\frac{d\varepsilon}{dt}$$

粘度 $\eta$ Viscosity




Time dependent




Deformation not reversible

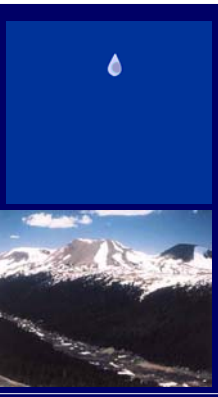


## Comparison

| elasticity | viscosity |
|---|---|
| Energy storage | Energy dissipation |
| Deformation recoverable | Not recoverable |
| Hook's solid | Newtonian liquid |
| $\sigma = E\varepsilon$ | $\sigma = \eta\dot{\gamma} = \eta\frac{d\varepsilon}{dt}$ |
| $E(\sigma,\varepsilon,T)$ | $E(\sigma,\varepsilon,T,t)$ |
| E is not time dependent | Time dependent |



## *All the materials are elastic and viscous.*

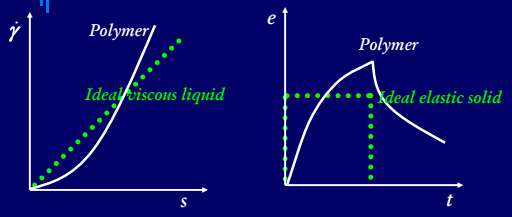


## 6.2.2
## Viscoelasticity of polymers

- During the deformation process of polymer material, viscosity and elasticity coexist.
- The stress σ is depending on the strain ε and strain rate $\dot{\varepsilon}$ at the same time.
- The mechanical property of polymers is a combination of that of ideal solid and ideal liquid.



## For polymers



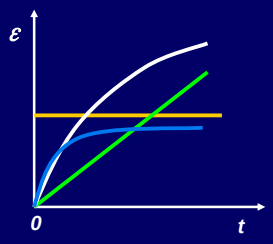

Non-Newtonian liquid

Different to the ideal solid



## Comparison

*σ = const.*




- Ideal viscous liquid
- Ideal elastic solid
- Linear polymer
- Crosslinked polymer



## *Review to the relaxation time τ*

Features of molecular motion

(1) Variety of molecular motion

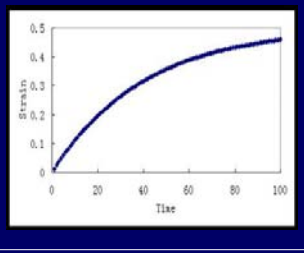
(2) Molecular motion is time-dependent

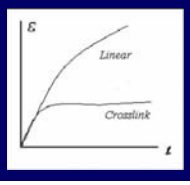
(3) Molecular motion is also temperature-dependent



## *Time-dependence*

$$\Delta x = \Delta x_0 e^{-t/\tau}$$




$$\varepsilon = \frac{\sigma_0}{E}(1 - e^{-t/\tau})$$



## *Temperature dependence*

*Arrhenius* equation

$$\tau = \tau_0 e^{\Delta E / RT}$$

*ΔE* – activation energy

T ↑ ⟷ τ ↓

T ↓ ⟷ τ ↑

## Relaxation or viscoelasticity

That the mechanical performance of polymer varies with time is called relaxation or viscoelasticity.

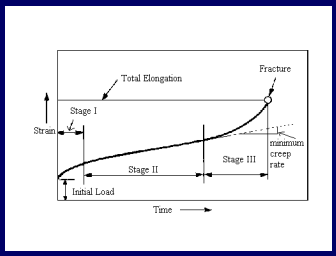
If the viscoelasticity of polymer can be described by combination of ideal elastic solid model and ideal viscous liquid model, it is the *Linear viscoelasticity*.

viscoelasticity
- Static — Creep, Stress relaxation
- dynamic — Hysteresis, Internal friction



## 6.2.3 Creep

Feature：small stress, long action time, deformation progresses continuously

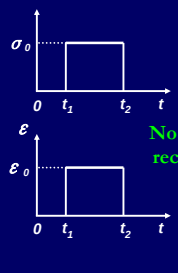



Creep of polymer reflects the stress resistance during long period.



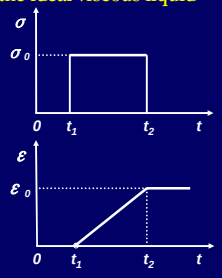
## Creep & creep recovery of ideal elastic solid and ideal viscous liquid

For the ideal elastic solid




No creep recovery

For the ideal viscous liquid

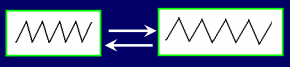


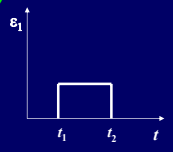



## THREE stages during polymer creep process

### (i) Ordinary elastic deformation ($\varepsilon_1$)

- Bond length and bond angle change spontaneously as the stress is applied on.
- The material obeys the Hook's law.
- Deformation of material is small and reversible.





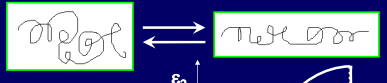

普弹形变示意图

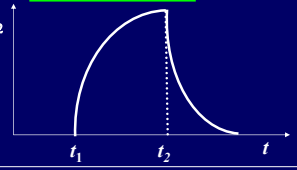
$$\varepsilon_1 = \frac{\sigma_0}{E_1} = D_1\sigma_0$$



### (ii) High elastic deformation ($\varepsilon_2$)

- High elastic deformation is caused by the motion of segments, larger than ordinary elastic deformation.
- Deformation needs time.
- Deformation restored gradually as the stress being released.



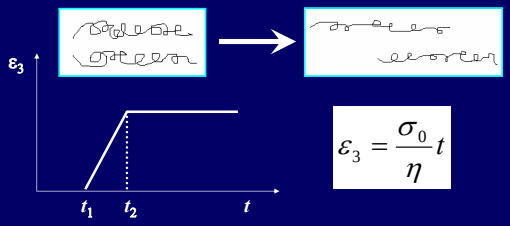



$$\varepsilon_2 = \frac{\sigma_0}{E_2}(1 - e^{-t/\tau})$$



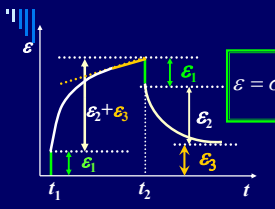
### (iii) viscous flow ($\varepsilon_3$)

- Slippage between polymer chains
- Deformation not recoverable




$$\varepsilon_3 = \frac{\sigma_0}{\eta}t$$

Three deformation occurs spontaneously as the polymer material is under stress




$$\varepsilon = \sigma_0[\frac{1}{E_1} + \frac{1}{E_2}(1 - e^{-t/\tau}) + \frac{t}{\eta}]$$

- As stress applies on, bond angle & length changes instantly
- Through motion of segments, conformation changes, deformation being enlarged
- Mass centers of molecules move



## About the action time

$$\varepsilon = \sigma_0[\frac{1}{E_1} + \frac{1}{E_2}(1 - e^{-t/\tau}) + \frac{t}{\eta}]$$

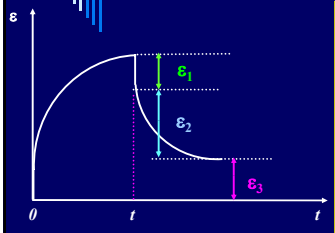
(A) Short action time (small *t*), the 2nd & 3rd items are closing to zero ⇒ $\frac{1}{E} = \frac{1}{E_1}$ ⇒ $E = E_1$

What can be inferred?

(B) Long action time (large *t*), the 2nd & 3rd items are larger than the 1st item. As the $t \to \infty$, the 2nd item $\to \sigma_0 / E_2 \ll$ the 3rd item ($\sigma_0 t/\eta$) ⇒ $\varepsilon = \sigma_0 \frac{t}{\eta}$



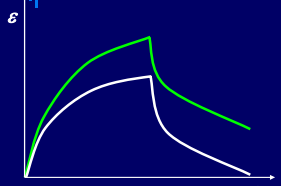
## Creep recovery




- At the moment that the stress is released, the secondary motion of chemical bonds stops instantly. Deformation recovers quickly.
- Through adjustment of conformation, deformation caused by entropy restored.
- Permanent movement of segments being left.



## Creep of linear & crosslinked polymer




Linear polymer

Crosslinked polymer

Deformation increases with time, no limitation;

Not recoverable.

Deformation increases up to a constant value;

Recoverable



## How to prevent creep?

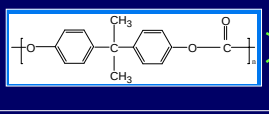
Nature of creep: movement of mass center

Interaction between chains?

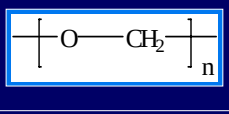
Crosslinking?

Flexibility?

PC, Polycarbonate

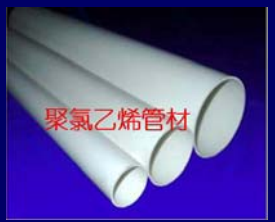


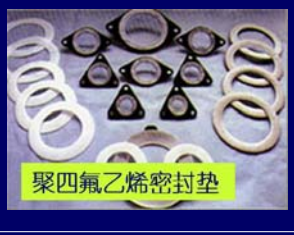
POM, Polyoxymethylene





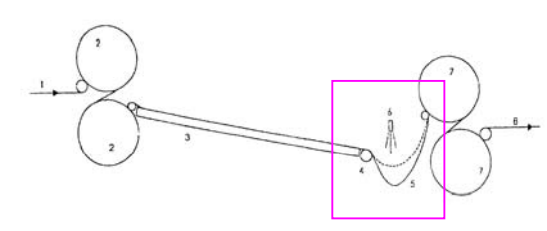
## Typical polymers be able to creep



## 6.2.4 Stress relaxation

Strain remains; internal stress released



Stress relaxation describes how polymers relieve stress under constant strain.



## Another type of stress relaxation

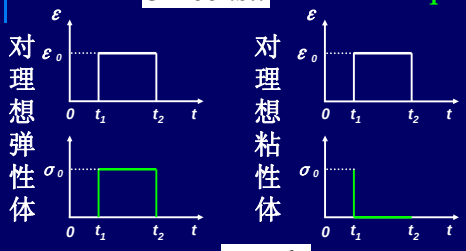
The body's natural relaxation response is a powerful antidote to stress.

身体的自然松弛反应是一剂解除压力的良药。



## Stress relaxation of ideal solids and ideal liquids

$\varepsilon = const.$




$\sigma = E\varepsilon$

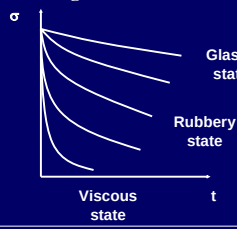
$\sigma = \eta \frac{d\varepsilon}{dt}$



## Stress relaxation – another form of molecular motion

- Similar to the creep, it is also transition of polymer chains from one balance state to another through molecular motion.

$\sigma = \sigma_0 e^{-t/\tau}$



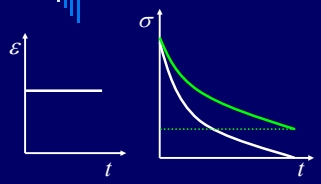

T >> Tg, there is almost no internal friction; molecules relax quickly; stress relaxation is not apparent

T << Tg, strong internal friction, slow relaxation, stress relaxation is not apparent too.

Near Tg, stress relaxation is apparent



## Stress relaxation of linear and crosslinked polymers




Linear

Crosslinked

No movement of mass center, stress relaxes to equilibrium value

Conformation reconstitute and slippage of chains are the nature of creep and stress relaxation of polymers



## 6.3 Linear viscoelasticity

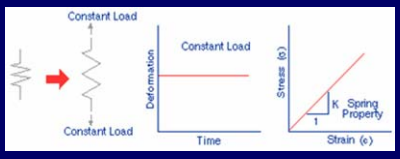
Which can be described by linear combination of Hook's solid & Newtonian Liquid.

Only phenomena are talking about, without consideration of the molecular motions

combination

- Serial connection
- Parallel connection

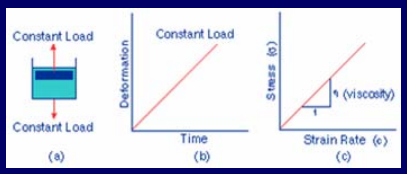
## *Ideal elastic solid* - Spring *弹簧*




**Hook's law** $\sigma_e = E\varepsilon_e$



## *Ideal viscous liquid* - Dashpot *粘壶*




**Newton's law** $\sigma_v = \eta \dfrac{d\varepsilon_v}{dt}$

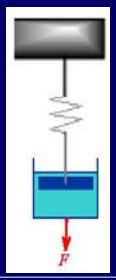


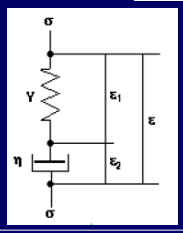
## 6.3.1 Maxwell element

**Serial**

Equal stresses $\sigma = \sigma_1 = \sigma_2$

Addition of strains $\varepsilon = \varepsilon_1 + \varepsilon_2$






## 例6-6

- 一高聚物的力学松弛行为可用Maxwell模型来描述，其参数为弹性模量 $E = 5 \times 10^5$ Pa, 粘度系数 $\eta = 5 \times 10^7$ Pa·s。外力作用并拉伸到原始长度的两倍，计算下面三种情况下的应力：
- （1）突然拉伸到原始长度的两倍，所需的应力；
- （2）维持到100秒时的应力；
- （3）维持到$10^5$秒时的应力。



$\sigma_1 = E\varepsilon_1 = \sigma_2 = \eta \dfrac{d\varepsilon_2}{dt} = \sigma$

应 力 等

应 变 加

应变速率加

$\dfrac{d\varepsilon}{dt} = \dfrac{d\varepsilon_1}{dt} + \dfrac{d\varepsilon_2}{dt}$

$\dfrac{d\varepsilon}{dt} = \dfrac{1}{E}\dfrac{d\sigma}{dt} + \dfrac{\sigma}{\eta}$

Maxwell 模型的运动方程



**Strain is constant,** $\dfrac{d\varepsilon}{dt} = 0$

**That is,** $\dfrac{1}{E}\dfrac{d\sigma}{dt} + \dfrac{\sigma}{\eta} = 0$

**Thus,** $\sigma(t) = \sigma(0)e^{-t/\tau}$

**Where,** $\tau = \dfrac{\eta}{E}$

$t = 0$ s

$\sigma(0) = E\varepsilon = 5.0\times10^5\times1 = 5.0\times10^5$（Pa）

$t = 100$ s

$\sigma(100) = 5.0\times10^5 e^{-100/100} = 5.0\times10^5\, e^{-1}$

$\approx 1.8\times10^5$（Pa）

$t = 10^5$ s

$\sigma(10^5) = 5.0\times10^5\, e^{-100000/100} \approx 0$



**It is shown that:**
**the stress decays gradually with time under constant strain.**

- At the moment the stress is applied on, spring deforms, but dash pot does not; stress is the maximum;
- At the moment $t = \tau = 100$ s, the stress lowers to the 1/e of the original one because of the viscous flow;
- At the moment $t \to \infty$, $\sigma \to 0$; total recovery of the spring deformation; residue strain provided by dash pot only.

Maxwell model can be use for description of stress relaxation.



## (1) Creep Analysis

$$\frac{d\varepsilon}{dt} = \frac{1}{E}\frac{d\sigma}{dt} + \frac{\sigma}{\eta}$$

$\sigma = const.$ $\quad \frac{d\sigma}{dt} = 0$

$$\frac{d\varepsilon}{dt} = \frac{\sigma}{\eta}$$

即Maxwell模型可以描述理想粘性体的蠕变响应

*Newton* liquid



## (2) Stress Relaxation Analysis

$$\frac{d\varepsilon}{dt} = \frac{1}{E}\frac{d\sigma}{dt} + \frac{\sigma}{\eta}$$

ε = const.

$$\frac{d\varepsilon}{dt} = \frac{1}{E}\frac{d\sigma}{dt} + \frac{\sigma}{\eta} = 0$$

$$\frac{1}{\sigma}d\sigma = -\frac{E}{\eta}dt$$

$t=0$, $\sigma=\sigma_0$

$$\int \frac{1}{x}dx = \ln x + C$$

$$\sigma(t) = \sigma_0 e^{-t/\tau} \qquad \tau = \eta/E$$

线型聚合物的应力松弛行为



## Relaxation time

What's the meaning of $\tau = \eta / E$ ?

单位 Unit

$\eta$ —— *Pa*·*s*

$E$ —— *Pa*

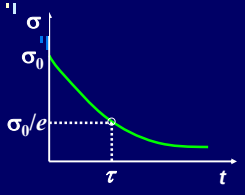
$\tau$ —— *s*

$\tau$是一个特征时间：松弛时间

$$\tau = \tau_0 e^{\Delta E/RT}$$



## *Physical meaning of* $\tau$




$$\sigma(t) = \sigma_0 e^{-t/\tau}$$

When $t = \tau$ $\quad \sigma(\tau) = \sigma_0 e^{-1}$

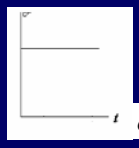
$$\sigma(\tau) = \frac{\sigma_0}{e} = 0.368\sigma_0$$

应力松弛到初始应力的0.368倍时所需的时间称为松弛时间。

当应力松弛过程完成63.2%所需的时间称为松弛时间。

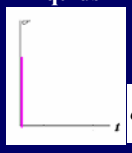
$\varepsilon = const.$

To the ideal solids



$\sigma = E\varepsilon$

To the ideal liquids



$\sigma = \eta \frac{d\varepsilon}{dt}$

应力松弛时间越短，松弛进行得越快；即
τ越小，越接近理想粘性；
τ越大，越接近理想弹性。



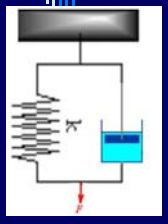
## Shortcomings of Maxwell element

（1） Maxwell model is not suitable for description of the creep of polymers. It describes the creep of ideal viscous liquids. (polymer is not ideal liquids)

（2）It is only suitable for the stress relaxation of linear polymer, not the crosslinked polymer, because no stress can be released to zero for crosslinked polymer.



## 6.3.2 *Kelvin* element

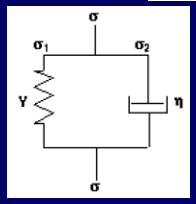


parallel

Equal strain; addition of stress

$\varepsilon = \varepsilon_e = \varepsilon_v$

$\sigma = \sigma_e + \sigma_v$






## Kinetic equation *运动方程*

$\sigma = \sigma_e + \sigma_v$ $\quad \varepsilon = \varepsilon_e = \varepsilon_v$

$\sigma_e = E\varepsilon_e$ $\quad \sigma_v = \eta \frac{d\varepsilon_v}{dt}$

$$\sigma(t) = E\varepsilon + \eta \frac{d\varepsilon}{dt}$$



## (1) Stress relaxation analysis

$\varepsilon = const.$ $\Rightarrow$ $\frac{d\varepsilon}{dt} = 0$

$$\sigma(t) = E\varepsilon + \eta \frac{d\varepsilon}{dt}$$

即Kelvin element
描述的是理想弹性体的应力松弛响应

$\sigma(t) = E\varepsilon$ Ideal elasticity



## (2) Creep analysis

$\sigma = const.$ $\quad \sigma = E\varepsilon + \eta \frac{d\varepsilon}{dt}$

$$\frac{\sigma}{E} = \varepsilon + \frac{\eta}{E}\frac{d\varepsilon}{dt} = \varepsilon + \tau \frac{d\varepsilon}{dt}$$

$\tau = \eta / E$

$\varepsilon(t) = Ae^{-t/\tau} + \frac{\sigma}{E}$

数学上以一阶非齐次常微分方程求解

For creeping $\sigma = \sigma_0$ $\quad t = 0$ $\quad \varepsilon = 0$

$A = -\frac{\sigma_0}{E}$ $\quad \varepsilon(t) = \frac{\sigma_0}{E}(1 - e^{-t/\tau})$

## 例6-7

- 一块橡胶，直径60mm，长度200mm，当作用力施加于橡胶下部，半个小时后拉长至300%(最大伸长600%)。问：(1)松弛时间？(2)如果伸长至400%，需多长时间？



（1） $\varepsilon(t)=\varepsilon(\infty)\left(1-e^{-t/\tau}\right)$ （蠕变方程）

已知 $\varepsilon(t)=300\%-100\%=200\%$

$\varepsilon(\infty)=600\%-100\%=500\%$

注意：ε为应变，而非伸长率λ，ε＝λ－1

$t=0.5h$

$\tau=0.98h=58.7\min$

（2） $300\%=500\%\left(1-e^{-t/0.98}\right)$

$t=0.90h=53.8\min$



$$\varepsilon(t)=\left(\frac{\sigma_0}{E}\right)\left(1-e^{-t/\tau}\right)$$

Ever seen before?

似曾相识?

令平衡形变

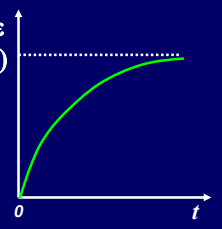
$$\varepsilon(\infty)=\frac{\sigma_0}{E} \Rightarrow \varepsilon(t)=\varepsilon(\infty)*\left(1-e^{-t/\tau}\right)$$

Is *Kelvin model* suitable for the creep of linear polymer?



## Discussion

$$\varepsilon(t)=\varepsilon(\infty)\cdot\left(1-e^{-t/\tau}\right)$$

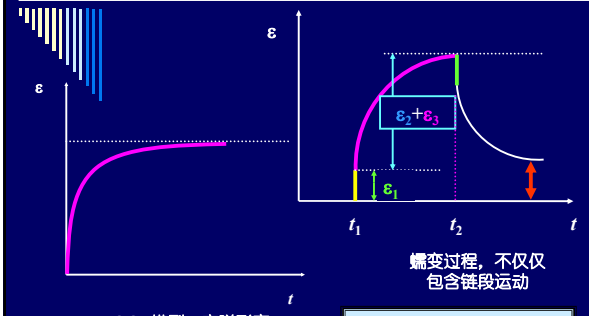



（1）t = 0, $e^{-t/\tau}=1$, ε(0)=0

（2）t ⇑, $e^{-t/\tau}$ ⇓, （1- $e^{-t/\tau}$ ） ⇑, ε(t) ⇑

（3）$t\to\infty$, ε(t) = ε(∞)






蠕变过程，不仅仅包含链段运动

Kelvin 模型－高弹形变，模拟链段运动

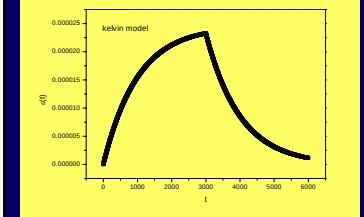
Kelvin 模型不能完整地描述高聚物的蠕变过程



蠕变回复

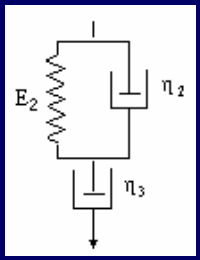
$\sigma=0$ $E\varepsilon+\eta\frac{d\varepsilon}{dt}=0$ $\frac{d\varepsilon}{\varepsilon}=-\frac{E}{\eta}dt=-\frac{dt}{\tau}$

$\varepsilon(t)=\varepsilon_0\cdot e^{-t/\tau}$ $t\to\infty$ $\varepsilon(\infty)\to 0$



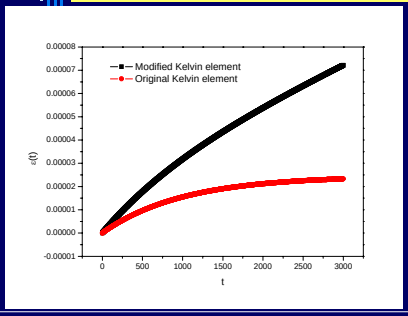

描述交联聚合物蠕变回复

例 6-8：一个kelvin单元($E = 2\times10^5 N\ m^{-2}$，$\tau = 10^3 s$)串联一个黏壶($\eta = 3\times10^8\ Pa\ s$)。加恒定负荷4.9 $N/m^2$，若负荷保留3000s，试画出蠕变曲线。






$$\varepsilon(t)=\frac{\sigma_0}{E}\left(1-e^{-t/\tau}\right)+\frac{\sigma_0}{\eta}t$$




作用时间越长，形变特征越接近于粘壶



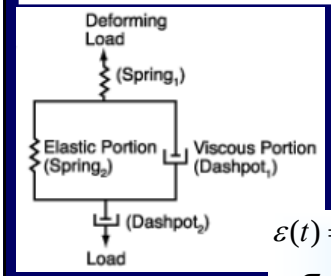
## Shortcomings of Kelvin element

（1） Not suitable for polymers in explanation of stress relaxation, but suitable for ideal elastic solids.

（2）Can not perfectly describe the creep of polymers, because deformation of polymer can not recover completely.

如何解决？



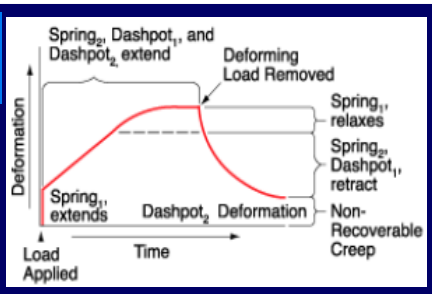



## 6.3.3 四元件模型

$$\varepsilon(t)=\varepsilon_1+\varepsilon_2+\varepsilon_3$$

$$=\frac{\sigma_0}{E_1}+\frac{\sigma_0}{E_2}(1-e^{-t/\tau})+\frac{\sigma_0}{\eta_3}t$$






四元件模型可以较完全的描述_____聚合物的 _____。



## 6.4 superposition principles

- 6.4.1 Boltzmann superposition principle
- 6.4.2 Time-temperature correspondence principle

## 6.4.1 Boltzmann superposition principle

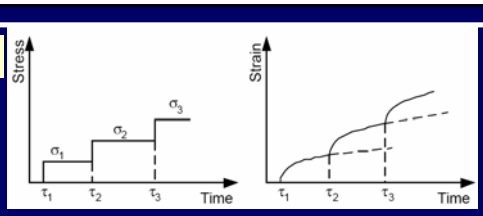
- It describes the response of a material to different loading histories.
- The Boltzmann superposition principle states that the response of a material to a given load is independent of the response of the material to any load, which is already on the material.
- The deformation of a specimen is directly proportional to the applied stress, when all deformations are compared to equivalent times.
- It is only valid in linear viscoelastic region.



## 6.4.1 Boltzmann superposition principle

- 聚合物力学行为的历史效应
  - 先前载荷历史对聚合物材料形变性能的影响
  - 试样的形变是负荷历史的函数
  - 多个载荷共同作用于聚合物时，其最终形变性能与个别载荷作用的关系
  - 每一项负荷步骤是独立的，而且彼此可以叠加






For the case of creep, the total strain may be expressed by

$$\varepsilon(t) = D(t-\tau_1)\sigma_1 + D(t-\tau_2)(\sigma_2-\sigma_1) + \cdots + D(t-\tau_i)(\sigma_i-\sigma_{i-1})$$

or

$$\varepsilon(t) = \int_{-\infty}^{t} D(t-\tau)d\sigma(t)$$

where $D(t)=1/E(t)$ is the compliance function, which is a characteristic of the polymer at a given temperature and initial stress



$\sigma D(t) = \varepsilon(t)$ 柔量 $D$

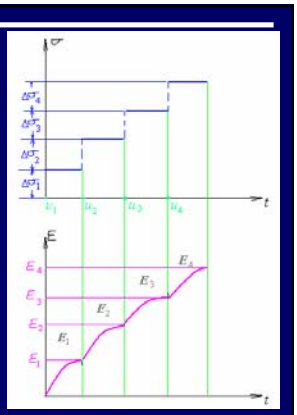
$$\varepsilon(t) = \varepsilon_1 + \varepsilon_2 + \ldots + \varepsilon_n = \sum_{i=1}^{n} \Delta\sigma_i D(t-u_i)$$

$\Delta\sigma_i$ – 应力的增量

$u_i$ – 施加力的时刻

连续化

$$\varepsilon(t) = \int_{-\infty}^{t} \left[\frac{\partial\sigma(u)}{\partial u}\right] D(t-u)du$$





## 例6-9

有一线型聚合物试样，其蠕变行为近似可用四元力学模型来描述，蠕变试验时先加一应力$\sigma = \sigma_0$，经5秒钟后将应力$\sigma$增加为2 $\sigma_0$，求到10秒钟时试样的形变值。已知模型的参数为：

- $\sigma_0 = 1\times10^8 N\ m^{-2}$
- $E_1 = 5\times10^8 N\ m^{-2}$
- $E_2 = 1\times10^8 N\ m^{-2}$
- $\eta_2 = 5\times10^8 Pa\ s$
- $\eta_3 = 5\times10^{10} Pa\ s$



高聚物的总形变为

$$\varepsilon(t) = \varepsilon_1 + \varepsilon_2 + \varepsilon_3 = \frac{\sigma_0}{E_1} + \frac{\sigma_0}{E_2}\left(1-e^{-t/\tau}\right) + \frac{\sigma_0}{\eta_3}\cdot t$$

其中 $\tau = \frac{\eta_2}{E_2} = \frac{1.0\times10^8}{1.0\times10^8} = 1s$

当应力 $\sigma_0 = 1.0\times10^8 Pa$ 时， 5s内的形变值

$$\varepsilon_0(5) = \frac{1\times10^8}{5.0\times10^8} + \frac{1\times10^8}{1\times10^8}\left(1-e^{-5/1}\right) + \frac{1\times10^8}{5\times10^{10}}\times5 = 1.203$$

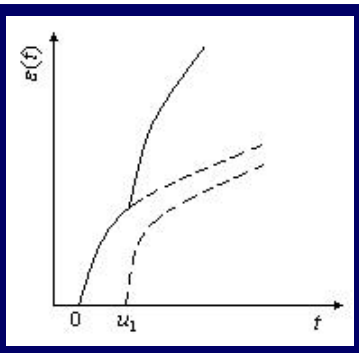
10s内形变值可用同样方法得到：

$$\varepsilon_0(10)=1.220$$

本题10秒时总形变等于0秒和5秒时相继加上的应力$\sigma_0$持续到10秒时所产生的形变的加和。根据Bolzmann原理

$$\varepsilon(10)=\varepsilon_0(10)+\varepsilon_0(5)$$
$$=1.220+1.203=2.423$$






相继作用在试样上的两个应力所引起的应变的线性加和



## 6.4.2 Time-temperature correspondence principle

The effect of rasing temperature is the same as prolonging the action (observation) time – time-temperature correspondence

反之亦然

BECAUSE 分子运动与温度、时间有关



Observation to some kind of mechanical response or relaxation

Low T, Long t

=

High T, Short t

Viscoelasticity of polymer at higher temperature within shorter time is equal to that at lower temperature within longer time

The molecular motion mechanism is the same



## *Application of T-t correspondence*

- To compare and convert the mechanical data obtained at different temperature or frequency, to obtain the result that can not be obtained in practice.
- For example
- Creep, may be observed for several years. By applying the T-t correspondence, the creep result obtained at higher temperature can be converted to lower temperature



## *以应力松弛下的松弛模量为例*

$$\sigma=E\varepsilon$$

$$\sigma(t)=\sigma(0)e^{-t/\tau} \Rightarrow E(t)=E(0)e^{-t/\tau}$$

At higher T, τ is smaller. For the same E, t is shorter;
However, at lower T, τ' is larger. For the same E, t' is longer;

$$E(t)=E(0)e^{-t/\tau}$$ Higher T

$$E'(t)=E(0)e^{-t'/\tau'}$$ Lower T

So, what is the shift factor?

Suppose $T_1 = 100°C$, $T_0 = 50\ °C$, obviously, $\tau_{100} < \tau_{50}$;

If the E(t) at $T_{50}$ is the same as that at $T_{100}$, then the observation time is longer;

$$E(t_{100}, T_{100}) = E(0)e^{-\frac{t_{100}}{\tau_{100}}} = E(t_{50}, T_{50}) = E(0)e^{-\frac{t_{50}}{\tau_{50}}}$$

$$\Rightarrow \frac{t_{100}}{\tau_{100}} = \frac{t_{50}}{\tau_{50}}$$

$$\Rightarrow t_{50} = \frac{\tau_{50}}{\tau_{100}} t_{100}$$

$$\Rightarrow \log t_{50} = \log\left(\frac{\tau_{50}}{\tau_{100}}\right) + \log t_{100}$$

$$\Rightarrow \log t_{50} - \log t_{100} = \log\left(\frac{\tau_{50}}{\tau_{100}}\right)$$

$$E'(t) = E(t) \Rightarrow e^{-(t'/\tau' - t/\tau)} = 1$$

$$\Rightarrow \frac{t'}{\tau'} = \frac{t}{\tau}$$

Shift factor

$\alpha_T = \tau'/\tau$

$$\Rightarrow t' = \frac{\tau'}{\tau} \cdot t$$

$$\Rightarrow \log t' = \log\left(\frac{\tau'}{\tau}\right) + \log t$$

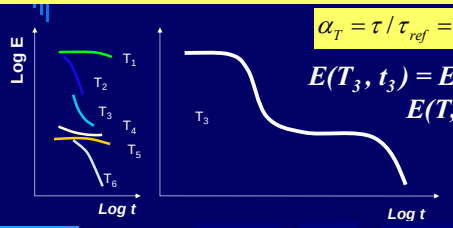


沿时间轴坐标发生平移，移动因子

$$\log(\alpha_T) = \log t(T) - \log t(T_{ref}) = \log \tau(T) - \log \tau(T_{ref})$$

$$\alpha_T = \tau / \tau_{ref} = t / t_{ref}$$

$E(T_3, t_3) = E(T, t) = E(T, t_3 \cdot a_T)$

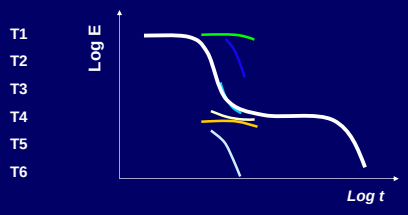



When $T<T_3$ ➡ $t>t_3$ ➡ $t_3 \cdot a_T > t_3$ ➡ $a_T > 1$ ➡ $lg a_T > 0$ ➡ 左移

When $T>T_3$ ➡ $t<t_3$ ➡ $t_3 \cdot a_T < t_3$ ➡ $a_T < 1$ ➡ $lg a_T < 0$ ➡ 右移



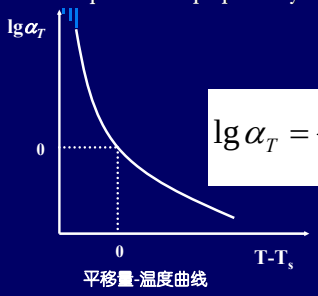
$T_1 < T_2 < T_3 < T_4 < T_5 < T_6$






It was proved by many experiments that the $\alpha_T$ - T relationship of lots of amorphous linear polymer was like this.

WLF equation was proposed by Williams, Landel and Ferry.




$$\lg \alpha_T = \frac{-C_1(T - T_s)}{C_2 + (T - T_s)}$$

When choosing different T as reference Ts, C1 and C2 vary.



When choosing $T_g$ as reference temperature, for the amorphous polymer

$c_1$=17.44, $c_2$=51.6

$$\lg a_T = \frac{-c_1(T - T_g)}{c_2 + (T - T_g)} = \frac{-17.44 \times (T - T_g)}{51.6 + (T - T_g)}$$

适用范围 $T_g \sim T_g+100$



例6-10

- 25℃下进行应力松弛实验，聚合物模量减少至$10^5 N/m^2$需要$10^7 h$。用WLF方程计算50℃和100 ℃下模量减少到同样值需要多久？假设聚合物的$T_g$是25℃。

$$\log\alpha_T = \log\frac{t50}{t25} = \frac{-17.44(50-25)}{51.6+50-25} = -5.69$$

$$\log\alpha_T^{'} = \log\frac{t100}{t25} = \frac{-17.44(100-25)}{51.6+100-25} = -10.33$$

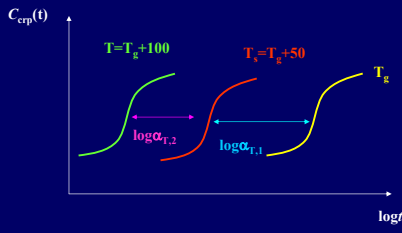
$$\log\frac{t50}{t25} = -5.69 = \log\frac{t50}{10^7}$$
$$\Rightarrow t50 = 10^{7-5.69} = 20.4(h)$$

$$\log\frac{t100}{t25} = -10.33 = \log\frac{t100}{10^7}$$
$$\Rightarrow t100 = 10^{7-10.33} = 4.65\times10^{-4}(h)$$



那么，若以$T_s = T_g + 50°C$为参考温度时，问$C_1$和$C_2$分别等于多少？

解：如图所示，分别以$T_g$和$T_s$为参考温度进行求解其余温度下函数的平移量$\log\alpha_T$






以$T_g$为参考温度时，据WLF方程，温度$T_s$和T下的函数变换到$T_g$时的平移量分别为

$$\log\alpha_{T,1} = \frac{-17.44\times(T_s-T_g)}{51.6+(T_s-T_g)} = \frac{-17.44\times50}{51.6+50} = -8.58$$

$$\log\alpha_{T,1} + \log\alpha_{T,2} = \frac{-17.44\times(T-T_g)}{51.6+(T-T_g)} = \frac{-17.44\times100}{51.6+100} = -11.5$$



以$T_s$为参考温度时，据WLF方程，温度$T_g$和T下的函数变换到$T_s$时的平移量分别为

$$\log\alpha'_{T,1} = \frac{-C_1\times(T_g-T_s)}{C_2+(T_g-T_s)} = \frac{-C_1\times(-50)}{C_2+(-50)} = -\log\alpha_{T,1} = 8.58$$

$$\log\alpha'_{T,2} = \frac{-C_1\times(T-T_s)}{C_2+(T-T_s)} = \frac{-C_1\times50}{C_2+50} = \log\alpha_{T,2} = -2.92$$

**联立求解$C_1$，$C_2$，得**

**$C_1$=8.86，$C_2$=101.6**



## 例6-11

- PMMA的力学损耗因子在130℃得到一峰值，假定测定频率是1周／秒．如果测定改在1000周／秒，在什么温度下得到同样的峰值?(已知PMMA的Tg＝105℃)



解：

$$\alpha_T = \frac{\tau_T}{\tau_g} = \frac{\omega_{T_g}}{\omega_T} \qquad \log\alpha_T = \log\frac{\omega_{T_g}}{\omega_T} = \frac{-17.44(T-T_g)}{51.6+T-T_g}$$

思路分析：130℃ $T_g$（105℃） ？（求）
1Hz ？（通过） 1000Hz

第一步：将测量从130℃、1Hz，移至105℃，求频率：

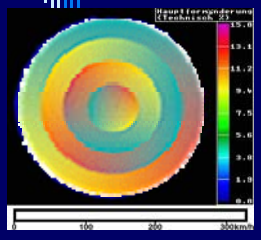
$$\log\frac{\omega_{105°}}{\omega_{130°}} = -5.69 \qquad \omega_{105°} = 2.03\times10^{-6}\,Hz$$

第二步：将测量从105℃、 $2.03\times10^{-6}\,Hz$ 移至1000Hz，求T

$$\log\frac{2.03\times10^{-6}}{10^3} = -8.69 = \frac{-17.44(T-105)}{51.6+T-105}$$

T＝156℃

## 6.5 Dynamic viscoelasticity 动态粘弹性



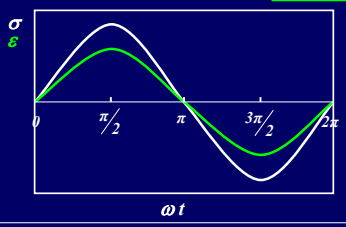
**Stress or strain varies periodically**



## (1) 用简单三角函数来表示

$$\sigma = \sigma_0 \sin \omega t$$

$$\varepsilon = \sigma / E = \frac{\sigma_0}{E} \sin \omega t$$




弹性响应

ε与σ完全同步

粘性响应??



## 粘性响应

$$\sigma = \eta \frac{d\varepsilon}{dt} + \sigma = \sigma_0 \sin \omega t \Rightarrow \eta \frac{d\varepsilon}{dt} = \sigma_0 \sin \omega t$$

$$\frac{\eta}{\sigma_0} d\varepsilon = \sin \omega t dt$$

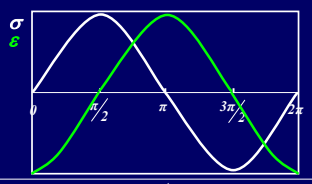
$$\int \sin u du = -\cos u + C$$

$$\frac{\eta}{\sigma_0} \varepsilon = -\cos \omega t / \omega$$

$$\varepsilon = -\frac{\sigma_0}{\eta \omega} \cos \omega t$$

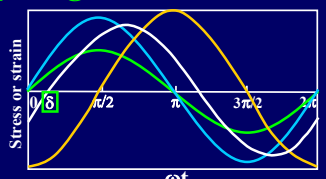
$$\varepsilon = \frac{\sigma_0}{\eta \omega} \sin(\omega t - \frac{\pi}{2})$$

滞后 π/2






## Comparing




$$\sigma = \sigma_0 \sin \omega t$$

$$\varepsilon = \frac{\sigma_0}{E} \sin \omega t$$

$$\varepsilon = \frac{\sigma_0}{\eta \omega} \sin(\omega t - \frac{\pi}{2})$$

$$\varepsilon = \varepsilon_0 \sin(\omega t - \delta)$$

$0 \le \delta \le \pi/2$



## (2) hysteresis

$$\sigma = \sigma_0 \sin \omega t$$

$$\varepsilon = \varepsilon_0 \sin(\omega t - \delta)$$

聚合物在交变应力作用下，应变落后于应力变化的现象称为滞后



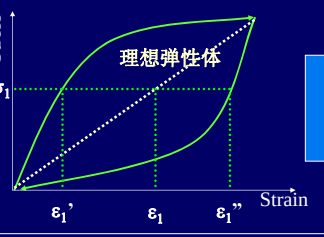
## Why hysteresis

Under stress, it will take a long time for the segments to reach a new equilibrium state through thermal movement (due to the internal friction). Hysteresis happens.

Frequency and temperature have great influence on the hysteresis of polymer.

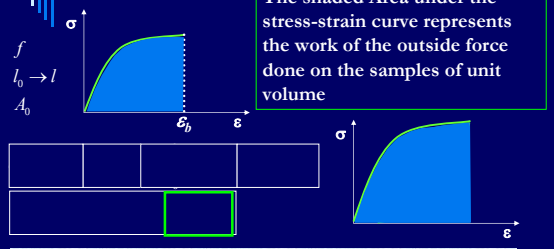
拉伸时滞后

回缩时也滞后



## Dissipated work ΔW

The shaded Area under the stress-strain curve represents the work of the outside force done on the samples of unit volume




面积大小为单位体积内材料在每一次拉伸-回缩循环中所消耗的功



## (3) 内耗 Internal friction (力学损耗)

$$\sigma = \sigma_0 \sin \omega t$$

$$\varepsilon = \varepsilon_0 \sin(\omega t - \delta)$$

展开

$$\varepsilon = \varepsilon_0 \sin \omega t \cos \delta - \varepsilon_0 \cos \omega t \sin \delta$$

类似于Hooke's solid, 相当于弹性

类似于Newton Liquid, 相当于粘性

链段间发生移动, 摩擦生热, 消耗能量, 所以称为内耗



## Definition of the internal friction

**The heat loss in every motion period**

运动每个周期中，以热的形式损耗掉的能量。

$$\Delta W = \pi \sigma_0 \varepsilon_0 \sin \delta$$

滞后的相角δ决定内耗

If $\delta = 0 \Rightarrow \Delta W = 0$

——all the energy are stored as elastic energy, no heat loss

If $\delta = 90^0 \Rightarrow \Delta W = \pi \sigma_0 \varepsilon_0$

——all the energy are dissipated



## Characterization of internal friction 内耗的表征

应变改写 $\varepsilon = \varepsilon_0 \sin \omega t$

应力表示 $\sigma = \sigma_0 \sin(\omega t + \delta)$

展开

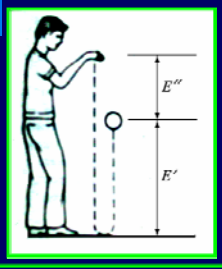
$$\sigma = \sigma_0 \cos \delta \sin \omega t + \sigma_0 \sin \delta \cos \omega t$$

完全同步，相当于弹性

相差90°，相当于粘性



## Dynamic modulus




$$E'' = \frac{\sigma_0}{\varepsilon_0} \sin \delta$$

$$E' = \frac{\sigma_0}{\varepsilon_0} \cos \delta$$

$$\sigma = E' \varepsilon_0 \sin \omega t + E'' \varepsilon_0 \cos \omega t$$



## 储能模量 E' 和损耗模量 E''

$$E^* = E' + iE''$$

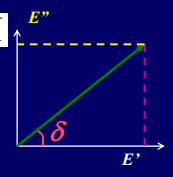
$i = \sqrt{-1}$

$$E' = \frac{\sigma_0}{\varepsilon_0} \cos \delta$$

反映弹性大小

$$E'' = \frac{\sigma_0}{\varepsilon_0} \sin \delta$$

反映内耗大小




复数模量图解

$$\sigma(t) = \sigma_0 \sin \omega t = \sigma_0 e^{i\omega t}$$

$$\varepsilon(t) = \varepsilon_0 \sin(\omega t - \delta) = \varepsilon_0 e^{i(\omega t - \delta)}$$

$$E^* = \frac{\sigma(t)}{\varepsilon(t)} = \frac{\sigma_0 e^{i\omega t}}{\varepsilon_0 e^{i(\omega t - \delta)}} = \frac{\sigma_0}{\varepsilon_0} e^{i\delta}$$

$$e^{i\delta} = \cos \delta + i \sin \delta$$

## Physical meanings

$E'$ 为实数模量或称储能模量，反映的是材料变形过程中由于弹性形变而储存的能量；

$E''$ 为虚数模量或称损耗模量，反映材料变形过程中以热损耗的能量

动态模量可写成 $E^* = E' + iE''$ 亦称为复数模量



## 损耗角正切

$E' = \frac{\sigma_0}{\varepsilon_0}\cos\delta$ $E'' = \frac{\sigma_0}{\varepsilon_0}\sin\delta$

$$tg\delta = \frac{E''}{E'}$$ 也可以用来表示内耗

δ =0， tg δ =0, 没有热耗散

δ =90°， tg δ = ∝, 全耗散掉

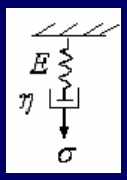


## 例6-12

- 推导弹簧-黏壶串联黏弹性模型的应力-应变方程及当模型施加正弦交变应力时的复数模量（E’，E’’）和复数柔量（J’，J’’）表达式。



（1）应力-应变方程：弹簧与黏壶串联模型即为如图所示的Maxwell模型。当一外力作用在模型上时，弹簧与黏壶所受的应力相同，总形变为两者的加和，即




$$\frac{d\varepsilon}{dt} = \frac{1}{E}\frac{d\sigma}{dt} + \frac{\sigma}{\eta}$$

Maxwell模型的运动方程



当模型受到一个交变应力 $\sigma(t) = \sigma_0 \exp(i\omega t)$ 作用时，其运动方程式可写成

$$\frac{d\varepsilon}{dt} = \frac{\sigma_0}{E} i\omega \exp(i\omega t) + \frac{\sigma_0}{\eta}\exp(i\omega t)$$

在$t_1$到$t_2$时间区内对上式积分，则

$$\varepsilon(t_2) - \varepsilon(t_1) = \frac{\sigma_0}{E}\left[\exp(i\omega t_2) - \exp(i\omega t_1)\right] + \frac{\sigma_0}{i\omega\eta}\left[\exp(i\omega t_2) - \exp(i\omega t_1)\right]$$

$$= \left(\frac{1}{E} + \frac{1}{i\omega\eta}\right)[\sigma(t_2) - \sigma(t_1)]$$



复合柔量

$$J^* = \frac{\varepsilon(t_2) - \varepsilon(t_1)}{\sigma(t_2) - \sigma(t_1)} = \frac{1}{E} + \frac{1}{i\omega\eta} = J - i\frac{J}{\omega\tau} = J' - iJ''$$

$$J' = J = \frac{1}{E} \qquad J'' = \frac{J}{\omega\tau} = \frac{1}{\omega\eta}$$

复合模量

$$E^* = \frac{\sigma(t_2) - \sigma(t_1)}{\varepsilon(t_2) - \varepsilon(t_1)} = \frac{1}{\frac{1}{E} + \frac{i}{\omega\eta}} = \frac{E\omega\tau}{\omega\tau - i}$$

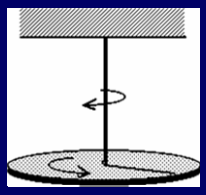
$$= \frac{E\omega^2\tau^2}{1+\omega^2\tau^2} + i\frac{E\omega\tau}{1+\omega^2\tau^2} = E' + iE''$$

因此，

$$E' = \frac{E\omega^2\tau^2}{1+\omega^2\tau^2} \qquad E'' = \frac{E\omega\tau}{1+\omega^2\tau^2}$$

## Measurement of internal friction

(1) *Torsional Pemdulum* 扭摆法





时效减量 $\Delta = \ln\frac{A_1}{A_2} = \ln\frac{A_2}{A_3} = \ldots$

——表示每次振幅所减小的幅度

推导得出 $tg\delta = \frac{\Delta}{\pi}$

振幅所减小的幅度小，即摆动持续时间长，$\Delta \to 0$， $tg\,\delta \to 0$, 热耗散小

振幅所减小的幅度大，即摆动持续时间短，$\Delta \to \infty$， $tg\,\delta \to \infty$, 热耗散大



## (2) Rheovibron and Autovibron

**DMA- Dynamic mechanical analysis 动态机械分析**



## 影响内耗的因素

（1） 温度

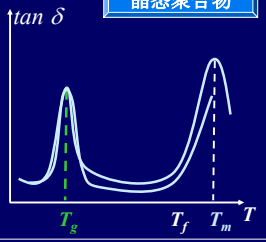
非晶态聚合物

晶态聚合物

•温度很高，运动单元运动快，应变能跟上应力变化，从而δ小， 内耗小

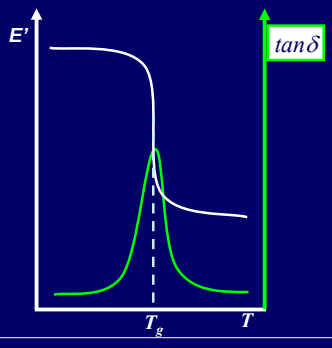
•温度很低，运动单元运动很弱，不运动，从而摩擦消耗的能量小，内耗小

•温度适中时，运动单元可以运动但跟不上应力变化，δ增大，内耗大






## DMTA results



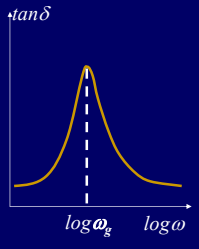



## (2) 频率

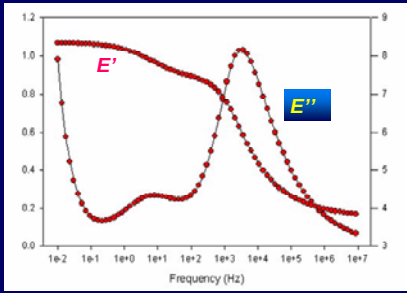
•频率很快，分子运动完全跟不上应力的交换频率，摩擦消耗的能量小， 内耗小。

•频率很慢，分子运动时间很充分，应变跟上应力的变化， δ小，内耗小。

•频率适中时，分子可以运动但跟不上应力频率变化，δ增大，内耗大。

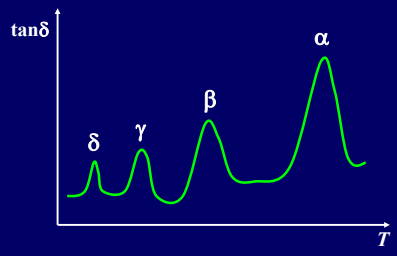


## DMA result - for frequency






## (3) 次级运动的影响



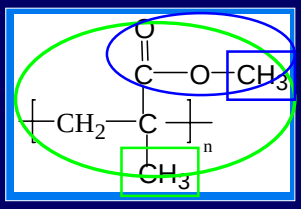

$T_g$ 和 $T_m$ 转变定认为α转变，其它的转变(松弛)过程按温度从高到低，依次叫β、γ、δ...，统称为次级松弛



## 用来分析分子结构运动的特点

e.g.

PMMA



α *Tg*转变

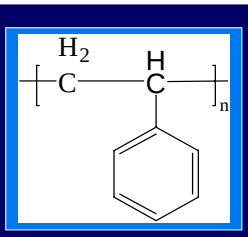
β 酯基的运动

γ 甲基的运动

δ 酯甲基的运动



## PS



α

β

γ

δ

α- *Tg*转变 373K

β- 苯基的转动 325K

γ- 曲柄运动 130K

δ- 苯基的振动 38~48K



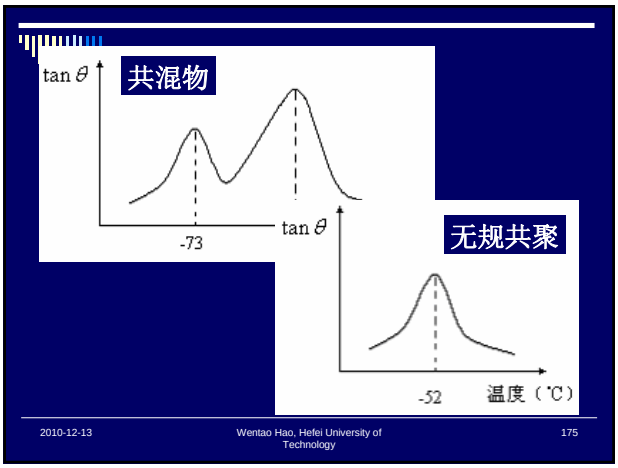
## For plastics

次级运动越多说明外力所做功可以通过次级运动耗散掉 ——抗冲击性能好



## 例3-8

- 现有A聚苯乙烯与顺丁橡胶的共混物（20:80重量比）；B苯乙烯与丁二烯无规共聚的丁苯橡胶（平均组成与共混物的组成相同）。试比较两种样品的力学损耗因子与温度的动态力学曲线。


共混物
tan θ
-73
tan θ
无规共聚
-52
温度（℃）