线性粘弹性

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△ 假设 $\underline{\underline{T}} = -p\underline{\underline{I}} + \underline{\underline{\tau}}$，$t$时刻 $\underline{\underline{\tau}}(t)$ 是 $t'<t$ 时刻的历史状态的线性叠加：

$$\boxed{\underline{\underline{\tau}}(\vec{r},t) = \int_{-\infty}^{t} \boxed{\frac{\partial}{\partial t'}\underline{\underline{\tau}}(\vec{r},t')} dt'}$$

其中，在 $t'\sim t'+dt'$ 时刻的偏应力张量增量可视为一个应变增量为 $\delta\underline{\underline{B}}$ 的应力松弛：

$$\delta\underline{\underline{B}} = \frac{\partial \underline{\underline{B}}}{\partial t'}dt' \ , \quad \frac{\partial \underline{\underline{B}}}{\partial t'} = \underline{\underline{L}}\,\underline{\underline{F}}\,\underline{\underline{F}}^T + \underline{\underline{F}}\,\underline{\underline{F}}^T\underline{\underline{L}}^T \ , \quad 当\ \underline{\underline{F}}\to\underline{\underline{I}}\ 时，\dot{\underline{\underline{B}}} = 2\underline{\underline{D}}$$

$$\therefore \frac{\partial}{\partial t'}\underline{\underline{\tau}}(\vec{r},t')\Big|_{\underline{\underline{F}}\to\underline{\underline{I}}} = G(t-t')\ 2\underline{\underline{D}}(t') \ ,$$

$G(t)$：应力松弛模量。不依赖应变

$$\boxed{\underline{\underline{\tau}} = 2\int_{-\infty}^{t} G(t-t')\,\underline{\underline{D}}(t')\,dt' \ , \quad \underline{\underline{F}}\to\underline{\underline{I}}}$$

线性粘弹性本构方程。

△ 无限小应变张量 $\underline{\underline{\varepsilon}} \overset{\text{def}}{=} \frac{1}{2}(\underline{\underline{F}}+\underline{\underline{F}}^T)$，应变张量依赖起始和终止时间 t', t，即

$$\underline{\underline{\varepsilon}} = \underline{\underline{\varepsilon}}(t',t)$$

$$\dot{\underline{\underline{\varepsilon}}} = \frac{1}{2}(\dot{\underline{\underline{F}}}+\dot{\underline{\underline{F}}}^T) = \frac{1}{2}(\underline{\underline{L}}\,\underline{\underline{F}} + (\underline{\underline{L}}\,\underline{\underline{F}})^T) \ , \quad 当\ \underline{\underline{F}}\to\underline{\underline{I}}\ 时\ \dot{\underline{\underline{\varepsilon}}}\to\underline{\underline{D}}$$

$$\therefore \underline{\underline{\varepsilon}}(t',t) = \int_{t'}^{t} \underline{\underline{D}}(t'')\,dt'' \ , \quad \underline{\underline{F}}\to\underline{\underline{I}}$$

$$\underline{\underline{\tau}} = -\int_{-\infty}^{t} M(t-t')\,\underline{\underline{\varepsilon}}(t,t')\,dt' \ , \quad M(t-t') = \frac{\partial G(t-t')}{\partial t'} \ , \quad \underline{\underline{F}}\to\underline{\underline{I}}$$

$M(t)$：记忆函数

△ 简单剪切下的振荡实验：

$$\underline{\underline{D}} = \frac{1}{2}\dot{\gamma}\begin{bmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix} \ , \quad \underline{\underline{\varepsilon}}(t,t') = \int_{t}^{t'} \underline{\underline{D}}(t'')\,dt'' = \frac{1}{2}\int_{t}^{t'}\dot{\gamma}(t'')\,dt'' \begin{bmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix}$$

观察此式可知，$\tau_{11}-\tau_{22} = \tau_{22}-\tau_{33} = 0$，法向应力差为零。无 Weissenberg 效应

$$\gamma(t) = \begin{cases} \gamma_0\sin(\omega t) \ , & t\geq 0 \\ 0 \ , & t<0 \end{cases} \qquad \dot{\gamma}(t) = \begin{cases} \gamma_0\omega\cos(\omega t) \ , & t\geq 0 \\ 0 & t<0 \end{cases}$$

$$\tau_{12} = \tau_{21} = \gamma_0\omega\int_{-\infty}^{t} G(t-t')\,\dot{\gamma}(t')\,dt'$$

$$= \gamma_0\omega\int_0^t G(u)\cos(\omega(t-u))\,du$$

$$= \gamma_0\omega\int_0^t G(u)\sin(\omega u)\,du\cdot\sin(\omega t) + \gamma_0\omega\int_0^t G(u)\cos(\omega u)\,du\cdot\cos(\omega t)$$

对于定常状态 $t\to\infty$，

$$\tau_{12} = \gamma_0\omega\left[\int_0^{\infty} G(u)\sin(\omega u)\,du\cdot\sin(\omega t) + \int_0^{\infty} G(u)\cos(\omega u)\cdot\cos(\omega t)\right]$$

定义储能模量和损耗模量

$$G'(\omega) \overset{\text{def}}{=} \omega\int_0^{\infty} G(u)\sin(\omega u)\,du, \qquad G''(\omega)\overset{\text{def}}{=} \omega\int_0^{\infty} G(u)\cos(\omega u)\,du$$

则 $\tau_{12} = \gamma_0\sqrt{G'^2(\omega)+G''^2(\omega)}\ \sin(\omega t+\delta(\omega))$

其中 $\tan\delta(\omega) = \dfrac{G''(\omega)}{G'(\omega)} > 0$，称损耗正切

构建复数值函数 $G^*(\omega) = G'(\omega) + i\,G''(\omega)$ 则

不依赖应变幅值γ_0

$\tau_{12} = \gamma_0\,|G^*(\omega)|\ \sin(\omega t+\delta(\omega)) \ = \sigma_0\sin(\omega t+\delta(\omega))$，$\sigma_0$：应力幅值

$|G^*(\omega)| = \sigma_0/\gamma_0$，$G'(\omega) = \dfrac{\sigma_0}{\gamma_0}\cos\delta$，$G''(\omega) = \dfrac{\sigma_0}{\gamma_0}\sin\delta$

定义 $\eta^*(\omega) = \eta'(\omega) - i\eta''(\omega)$，$\eta'(\omega) = G''(\omega)/\omega$，$\eta''(\omega) = G'(\omega)/\omega$

G^*，η^* 分别称复数模量和复数粘度。

△ 在线性粘弹性的构建中我们采用了仅在无穷小形变($\underline{\underline{F}}\to\underline{\underline{I}}$)才满足标架变换不变性的无穷小应变张量$\underline{\underline{\varepsilon}}$。我们尝试改用具有标架变换不变性的应变张量$\underline{\underline{B}}$，同样通过Boltzmann叠加，构建本构关系结果如下：

设在 $t'\sim t'+dt'$ 微时元内的有限应变张量$\underline{\underline{B}}$有增量

$$\frac{\partial}{\partial t'}\underline{\underline{B}}\,dt' = \dot{\underline{\underline{B}}}\,dt' \qquad \text{(注意此处的时间偏导数不保持客观性)}$$

该应变增量相当于叠加一应力松弛：

$$d\underline{\underline{\tau}}(t') = G(t-t')\,\dot{\underline{\underline{B}}}(t')\,dt' \qquad (\text{一般地 } \dot{\underline{\underline{B}}}\neq 2\underline{\underline{D}})$$

则 t 时刻的偏应力张量

$$\underline{\underline{\tau}}(t) = \int_{-\infty}^{t} G(t-t')\,\dot{\underline{\underline{B}}}(t')\,dt' = -\int_{-\infty}^{t} M(t-t')\,\underline{\underline{B}}(t,t')\,dt', \quad \underline{\underline{B}}(t,t') = \int_t^{t'}\dot{\underline{\underline{B}}}(t'')\,dt''$$

该模型称 Lodge 模型，Lodge (1956) Trans. Faraday Soc. 52:120

△ 简单剪切场

$$\underline{\underline{B}} = \begin{pmatrix} 1+\gamma^2 & \gamma & 0 \\ \gamma & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \qquad \begin{aligned} \tau_{12} = \tau_{21} &= \int_{-\infty}^{t} M(t-t')\,\gamma(t,t')\,dt' = \int_{-\infty}^{t} G(t-t')\,\dot\gamma(t')\,dt' \\ \tau_{11}-\tau_{22} &= \int_{-\infty}^{t} M(t-t')\,\gamma^2(t,t')\,dt', \quad \tau_{22}-\tau_{33} = 0 \end{aligned}$$

其中利用了 $\dot\gamma(t') = \dfrac{\partial}{\partial t'}\gamma(t,t') = \dfrac{\partial}{\partial t'}\displaystyle\int_t^{t'}\dot\gamma(t'')\,dt''$

振荡剪切的第一法向应力差：$\gamma(t) = \begin{cases} \gamma_0\sin(\omega t), & t\geq 0 \\ 0, & t<0 \end{cases}$

$$\tau_{11}-\tau_{22} = -\int_{-\infty}^{t} M(t-t')\,\gamma^2(t,t')\,dt' = \cdots$$

$$= \gamma_0^2\left[\tfrac{1}{2}G''(2\omega) - G''(\omega)\right]\sin(2\omega t) + \gamma_0^2\left[G'(\omega) - \tfrac{1}{2}G'(2\omega)\right]\cos(2\omega t) - \gamma_0^2 G'(\omega)$$

$$\overset{\text{def}}{=} \Psi_1\,\dot\gamma_0^2$$

其中

$$\Psi_1 = \frac{G'(\omega)}{\omega^2} - \left[\frac{G''(2\omega)}{2\omega^2} - \frac{G''(\omega)}{\omega^2}\right]\sin(2\omega t) - \left[\frac{G'(\omega)}{\omega^2} - \frac{G'(2\omega)}{2\omega^2}\right]\cos(2\omega t)$$

$$= \Psi_1^d + \Psi_1'\cos(2\omega t) + \Psi_1''\sin(2\omega t)$$

$$\Psi_1^d = \frac{G'(\omega)}{\omega^2} = \eta''(\omega)/\omega, \quad \Psi_1' = -\frac{G''(2\omega)}{2\omega^2} - \frac{G''(\omega)}{\omega^2} = -[\eta''(2\omega) - \eta''(\omega)]/\omega$$

$$\Psi_1'' = -\frac{G'(\omega)}{\omega^2} - \frac{G'(2\omega)}{2\omega^2} = -[\eta'(\omega) - \eta'(2\omega)]/\omega$$

$$\Psi_1^d = \frac{G'(\omega)}{\omega^2} = \eta''(\omega)/\omega \,, \quad \Psi_1' = -\frac{G''(2\omega)}{2\omega^2} - \frac{G''(\omega)}{\omega^2} = -[\eta''(2\omega) - \eta''(\omega)]/\omega$$

$$\Psi_2 = -\frac{G'(\omega)}{\omega^2} - \frac{G'(2\omega)}{2\omega^2} = -[\eta'(\omega) - \eta'(2\omega)]/\omega$$

△ 记忆函数的一般形式：

Maxwell 模型： $\underline{\underline{\tau}} = \int_{-\infty}^{t} (\eta/\lambda) \, 2\underline{\underline{D}}(t') \, e^{-(t-t')/\lambda} dt'$， $\lambda \dot{\underline{\underline{\tau}}} + \underline{\underline{\tau}} = 2\eta \underline{\underline{D}}$

$G(t) = \frac{\eta}{\lambda} e^{-t/\lambda}$ 　 Lodge 模型： $\underline{\underline{\tau}} = \int_{-\infty}^{t} \frac{\eta}{\lambda} e^{-(t-t')/\lambda} \underline{\underline{B}}(t,t') dt'$， $\lambda \overset{\nabla}{\underline{\underline{\tau}}} + \underline{\underline{\tau}} = 2\eta \underline{\underline{D}}$

拉伸指数： $G(t) = G_0 \exp(-(t/\lambda)^\beta)$

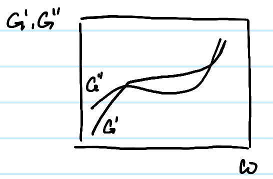
Kohlrausch－Williams－Watts (KWW) 函数

广义 Maxwell： $G(t) = \sum_{i=1}^{N} g_i e^{-t/\lambda_i}$

当 $N \to \infty$， $G(t) = \int_0^\infty \frac{H(\lambda)}{\lambda} e^{-t/\lambda} d\lambda = \int_0^\infty H(\lambda) e^{-t/\lambda} d\ln\lambda$

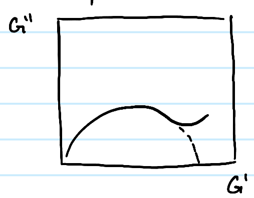
其中 $H(\lambda)$ 称松弛时间谱。

△ 作图方法：(以线性聚合物熔体为例)



van Gurp－Palman plot：

Cole－Cole plot



relaxation time spectrum：