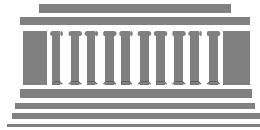


Linear Viscoelasticity:

A Survey of Some Essential Features

G. C. Berry

Department of Chemistry

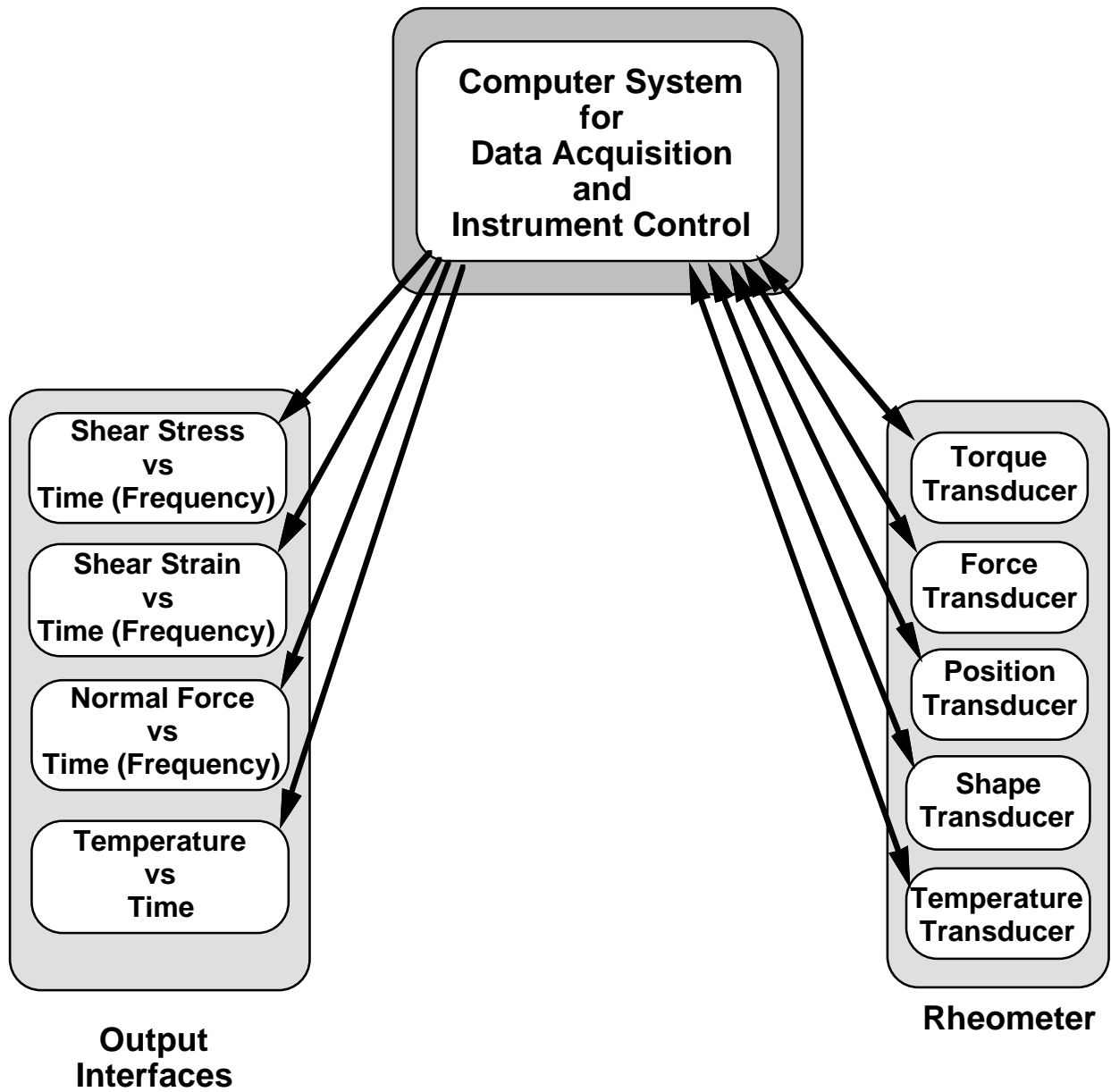


Carnegie Mellon University

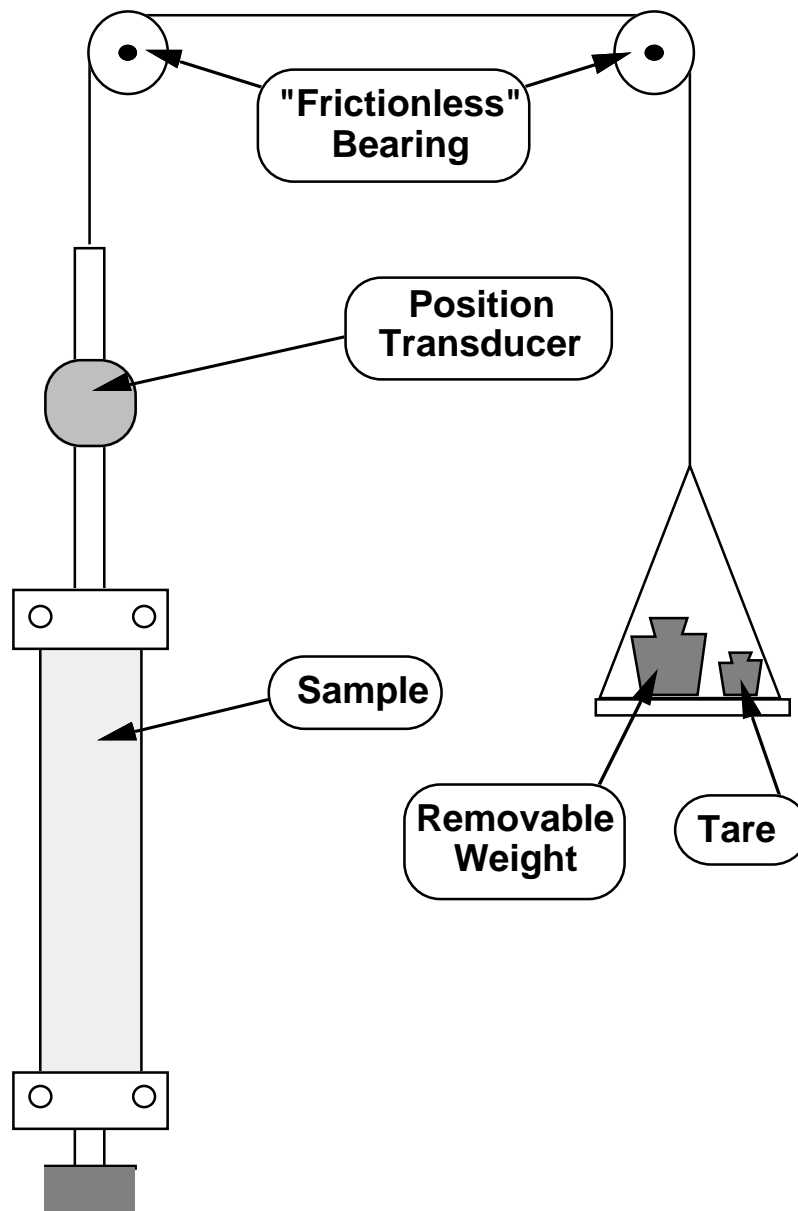
Lecture Notes available at the web site:
www.chem.cmu.edu/Berry/workshop.pdf

e-mail: gcberry@andrew.cmu.edu

Schematic of Rheometer System

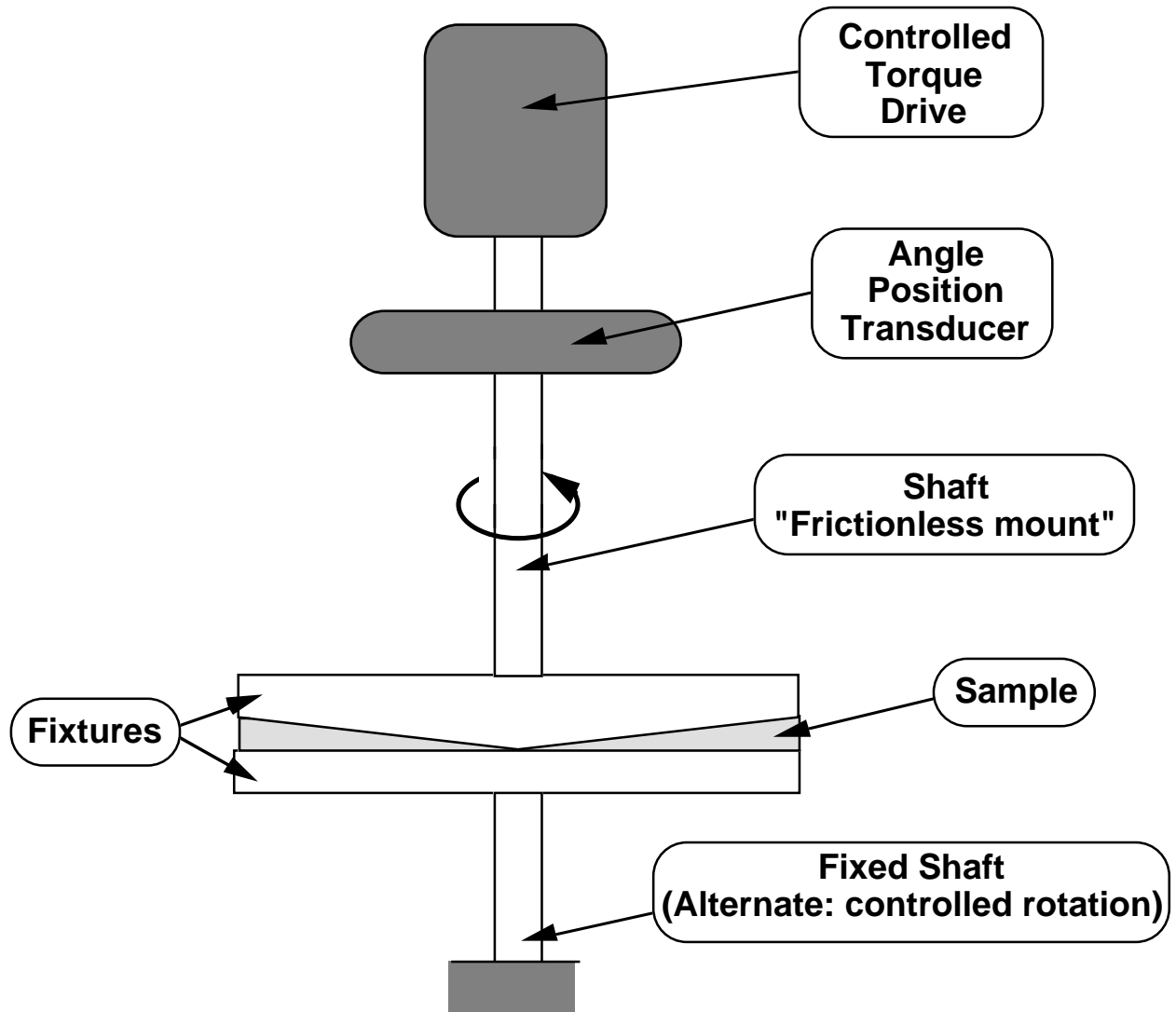


TENSILE CREEP AND RECOVERY



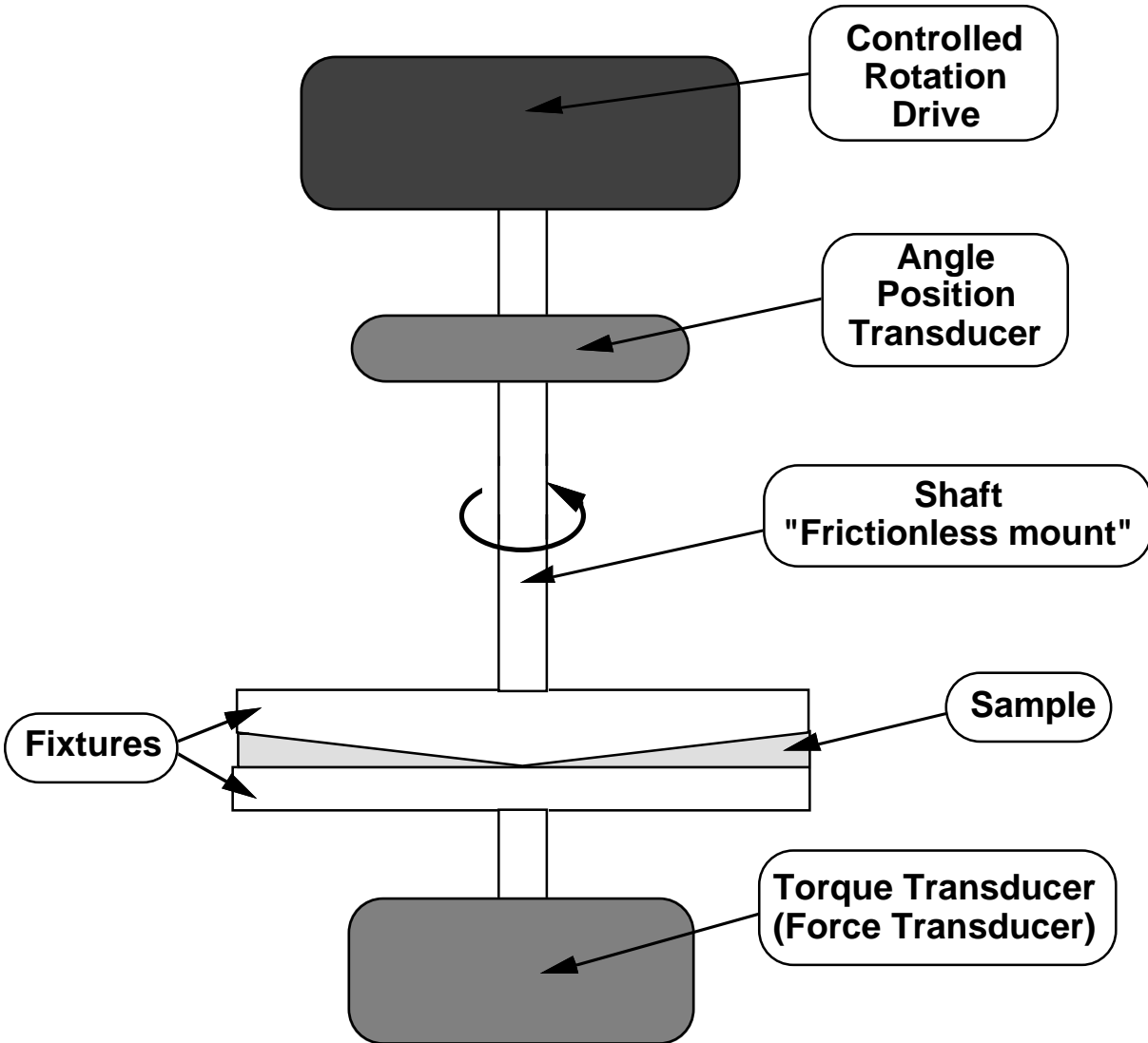
Device	Input	Output
Removable Weight	Controlled weight	Controlled force
Position Transducer	Measure of shaft position	Voltage (current)

CONTROLLED STRESS RHEOMETER



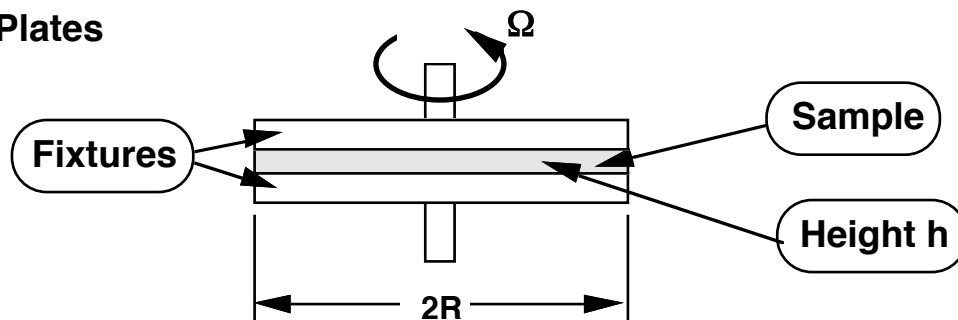
Device	Input	Output
Controlled Torque Drive	Controlled voltage	Controlled torque
Angle Position Transducer	Measure of shaft angle	Voltage (current)

CONTROLLED DEFORMATION RHEOMETER

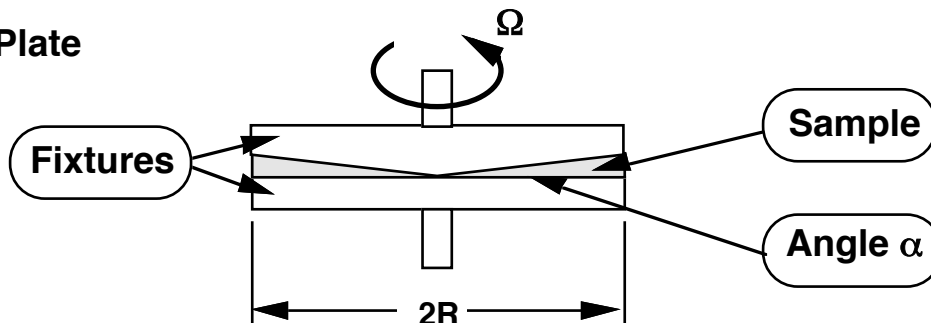


Device	Input	Output
Controlled Deformation Drive	Controlled voltage	Controlled shaft rotation
Angle Position Transducer	Measure of shaft angle	Voltage (current)
Torque Transducer	Measure of torque	Voltage (current)
Normal Force Transducer	Measure of Force	Voltage (current)

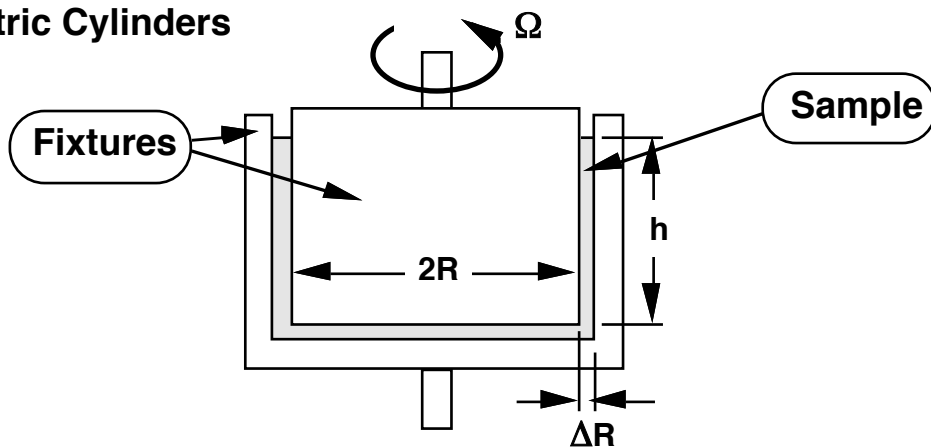
Parallel Plates



Cone & Plate



Concentric Cylinders



Geometry	Measured	Calculated
Parallel Plate	Torque: M	Stress: $S = (2r/R)M/\pi R^3$
Parallel Plate	Rotation: Ω	Strain: $\gamma(r) = (r/h) \Omega$
Cone & Plate	Torque: M	Stress: $S = (3/2)M/\pi R^3$
Cone & Plate	Rotation: Ω	Strain: $\gamma = (1/\alpha) \Omega$
Concentric Cylinder	Torque: M	Stress: $S \approx (R/2h)M/\pi R^3$
Concentric Cylinder	Rotation: Ω	Strain: $\gamma \approx (R/\Delta R) \Omega$

Compliance = Strain/Stress

Modulus = Stress/Strain

Linear Viscoelastic Functions:

Shear Compliance	$J(t)$
Shear Modulus	$G(t)$
Bulk Compliance	$B(t)$
Bulk Modulus	$K(t)$
Tensile Compliance	$D(t) = J(t)/3 + B(t)/9$
Tensile Modulus	$E(t) = \{3/G(t) + 9/K(t)\}^{-1}$

Incompressibility approximation:

$$K(t) \gg G(t) \approx E(t)/3$$

$$B(t) \ll J(t) \approx D(t) \times 3$$

Relationship between Compliances and Moduli:

$$\frac{1}{t} \int_0^t ds G(t-s) J(s) = 1$$
$$\frac{1}{t} \int_0^t ds K(t-s) B(s) = 1$$

Linear Viscoelastic Constitutive Equations:

$$\varepsilon_{ij} = \frac{1}{2} \left(\frac{\partial u_i}{\partial x_j} + \frac{\partial u_j}{\partial x_i} \right)$$

$$2\varepsilon_{ij}(t) = \int_{-\infty}^t ds \left\{ J(t-s) \left[\frac{\partial S_{ij}(s)}{\partial s} - \frac{1}{3} \delta_{ij} \frac{\partial S_{\alpha\alpha}(s)}{\partial s} \right] + \frac{2}{9} \delta_{ij} B(t-s) \frac{\partial S_{\alpha\alpha}(s)}{\partial s} \right\}$$

$$S_{ij}(t) = \int_{-\infty}^t ds \left\{ G(t-s) \left[2 \frac{\partial \varepsilon_{ij}(s)}{\partial s} - \frac{2}{3} \delta_{ij} \frac{\partial \varepsilon_{\alpha\alpha}(s)}{\partial s} \right] + \delta_{ij} K(t-s) \frac{\partial \varepsilon_{\alpha\alpha}(s)}{\partial s} \right\}$$

The Shear Compliance:

Strain: $\gamma(t) = 2 \varepsilon_{12}(t)$

Stress: $\sigma(t) = S_{12}(t)$

$$\gamma(t) = \int_{-\infty}^t ds J(t-s) \frac{\partial \sigma(s)}{\partial s}$$

$$\sigma(t) = \int_{-\infty}^t ds G(t-s) \frac{\partial \gamma(s)}{\partial s}$$

The Shear Compliance:

$$J(t) = J_o + [J_s - J_o]\psi(t) + t/\eta$$

$$J(t) = J_s - [J_s - J_o]\alpha(t) + t/\eta$$

Three parameters and a function of time;

$$\alpha(t) = 1 - \psi(t); \alpha(0) = 1 \text{ and } \alpha(\infty) = 0$$

$$\text{Solid: } 1/\eta = 0; J_s G_e = 1$$

$$\text{Fluid: } \eta > 0; J_s \geq J_o > 0$$

The Shear Modulus:

$$G(t) = G_e + [G_o - G_e]\phi(t)$$

Two parameters and a function of time;

$$\phi(0) = 1 \text{ and } \phi(\infty) = 0; G_o J_o = 1$$

$$\text{Solid: } J_s G_e = 1; \int_0^\infty du \phi(u) = \text{constant}$$

$$\text{Fluid: } G_e = 0; G_o \int_0^\infty du \phi(u) = \eta; G_o \int_0^\infty du u \phi(u) = J_s \eta^2$$

Relation to Dynamic Functions:

A special case, with sinusoid deformation

$$J'(\omega) = J_s - [J_s - J_o]\omega \int_0^\infty du \alpha(u) \sin(\omega u)$$

$$J''(\omega) = (\omega\eta)^{-1} + [J_s - J_o]\omega \int_0^\infty du \alpha(u) \cos(\omega u)$$

$$G'(\omega) = J'(\omega) / \{J'(\omega)^2 + J''(\omega)^2\}$$

$$G''(\omega) = J''(\omega) / \{J'(\omega)^2 + J''(\omega)^2\}$$

$$\tan \delta(\omega) = J''(\omega) / J'(\omega) = G''(\omega) / G'(\omega)$$

Low Frequency Limits:

$$G''(\omega) = \omega\eta - \dots = \tau_c / J_s - \dots$$

$$G'(\omega) = (\omega\eta)^2 J_s + \dots = \tau_c^2 / J_s - \dots$$

$$J'(\omega) = J_s - \dots$$

$$J''(\omega) = (\omega\eta)^{-1} - \dots$$

Molecular Parameters:

- L: contour length ($M_L = M/L$)
- R_G : radius of gyration (root-mean-square)
- R_H : hydrodynamic radius ($R_H = \Xi/6\pi\eta_{\text{LOC}}^{(c)}$)
- $\eta_{\text{LOC}}^{(c)}$: local viscosity

$$[\eta] = [\eta]_{\text{FD}} K_\eta R_H/L$$

$$[\eta]_{\text{FD}} = \pi N_A R_G^2/M_L$$

Thermodynamic Interactions:

For the wormlike model for a semiflexible chain:

$$R_G \approx \{ (\hat{a}L\alpha^2/3)^{-1} + (L^2/12)^{-1} \}^{-1/2}$$

\hat{a} : persistence length

α : expansion factor

$$\alpha \approx \left(1 + \hat{z} + k_\alpha (\hat{z}/2)^2 \right)^{\nu-1/2}; \quad \nu \approx 3/5$$

$$\hat{z} = a_1 A (\hat{a}/L) z / (2\nu - 1)$$

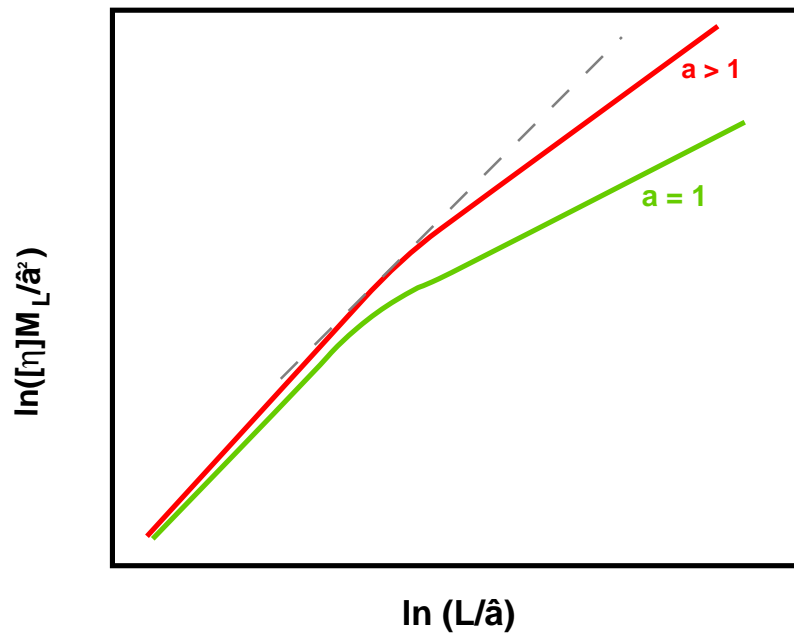
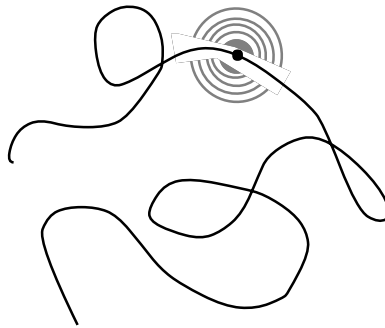
$$z = (3d_T/16\hat{a})(3L/\pi\hat{a})^{1/2} \approx 0.18(d_T/\hat{a})(L/\hat{a})^{1/2}$$

Hydrodynamic Interaction:

$$K_{\eta} R_H \approx \left\{ \left[\frac{10}{3} (R_H)_{ND} \right]^{-2} + \left[(R_H)_{FD} \right]^{-2} \right\}^{-1/2}$$

where

$$(R_H)_{ND}/L = \{2 \cdot 3^{1/2}/9\} (\hat{a}/L)^{1/2} \alpha; \quad (R_H)_{FD}/L \approx 1$$



Dimensionless reduced viscosity $\tilde{\eta}$:

$$\tilde{\eta} = \frac{\eta}{\eta_{LOC}^{(c)}} = 1 + c[\eta]^{(c)}$$

- $[\eta]^{(c)}$ is a function of c , L and \hat{a}
 $[\eta]^{(c)}$ at infinite dilution
 $[\eta]^{(c)}$ $[\eta]_{FD}$ with increasing c , excluding entanglements
- $\eta_{LOC}^{(c)}$ is a "Local viscosity"
 $\eta_{LOC}^{(c)}$ solvent at infinite dilution
 $\eta_{LOC}^{(c)}$ repeat, repeat unit "viscosity" for pure polymer

Following Arrhenius (1887):

$$\eta_{LOC}^{(c)} = \eta_{solvent}^{1-\mu} \eta_{repeat}^{\mu} ; \mu$$

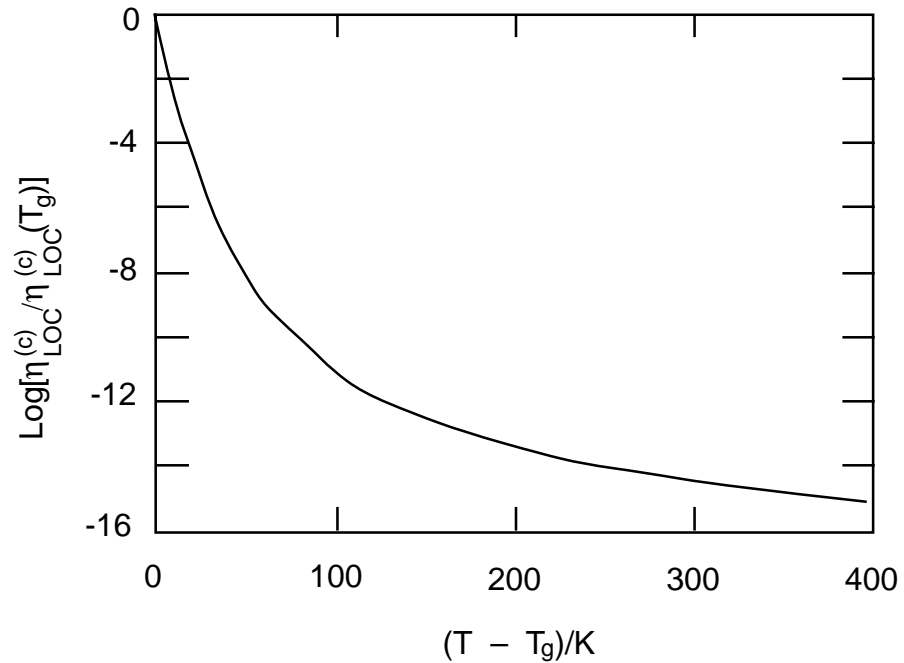
For small c : $\eta_{LOC}^{(c)} \approx \eta_{solvent} \exp(b c)$

In general, for either solvent or repeat:

$$\mu = \frac{\exp\left(\frac{W_{\mu}}{T}\right)}{\exp\left(\frac{W_{\mu}}{T}\right) + \exp\left(\frac{K}{T - (T_g)_{\mu}}\right)}$$

with K and W_{μ} both (essentially) universal constants.

Behavior for $\Delta = 57.5$ K and $K = 2300$ K:



T_g depends on the volume fraction ϕ of polymer:

$$T_g^{-1} \approx \phi T_{g; \text{poly}}^{-1} + (1 - \phi) T_{g; \text{solv}}^{-1}$$

T_g is also a weak function of M for small M .

$$\eta(T_g) \approx 10^{9-12} \text{ Pa}\cdot\text{s}$$

Several regimes of viscoelastic behavior are related to the mean separation Λ of molecular centers relative to the root-mean-square radius of gyration R_G :

$$\Lambda = (M/cN_A)^{1/3}$$

- The distribution of molecular centers is liquid-like
- $\alpha^{(c)}$ decreases toward unity with decreasing Λ/R_G for coils
($\alpha^{(c)} \approx \text{MAX}\{1; \alpha(1 + [7(R_G/\Lambda)^3]^2) - 1/16\}$)
- $K_\eta^{(c)}R_H^{(c)}/L$ increases toward unity with decreasing Λ/R_G
- $[\eta]^{(c)}$ increases from $[\eta]$ toward $[\eta]_{FD}^{(c)}$:
(In the absence of chain entanglements)

$$[\eta]_{FD}^{(c)} = \pi N_A (R_G \alpha^{(c)})^2 / M_L$$

Approximate relation (no chain entanglements):

$$[\eta]^{(c)} \approx \{[\eta](1 + c[\eta])^{k'}\}^2 + \{(c/\rho)^\beta [\eta]_{FD}^{(c)}\}^2\}^{1/2}$$

$$0 \leq \beta \leq k'$$

Chain entanglements act to increase $K^{(c)}$ $R^{(c)}$:

$$[\eta]^{(c)} = \left\{ [\eta]^{(c)} (1 + c[\eta]^{(c)})^{k'} \right\}^2 + \left\{ (c/c_{FD}) [\eta]^{(c)}_{FD} E(\tilde{X}/\tilde{X}_c) \right\}^2 \right\}^{1/2}$$

$$\tilde{X} = c[\eta]^{(c)}_{FD}$$

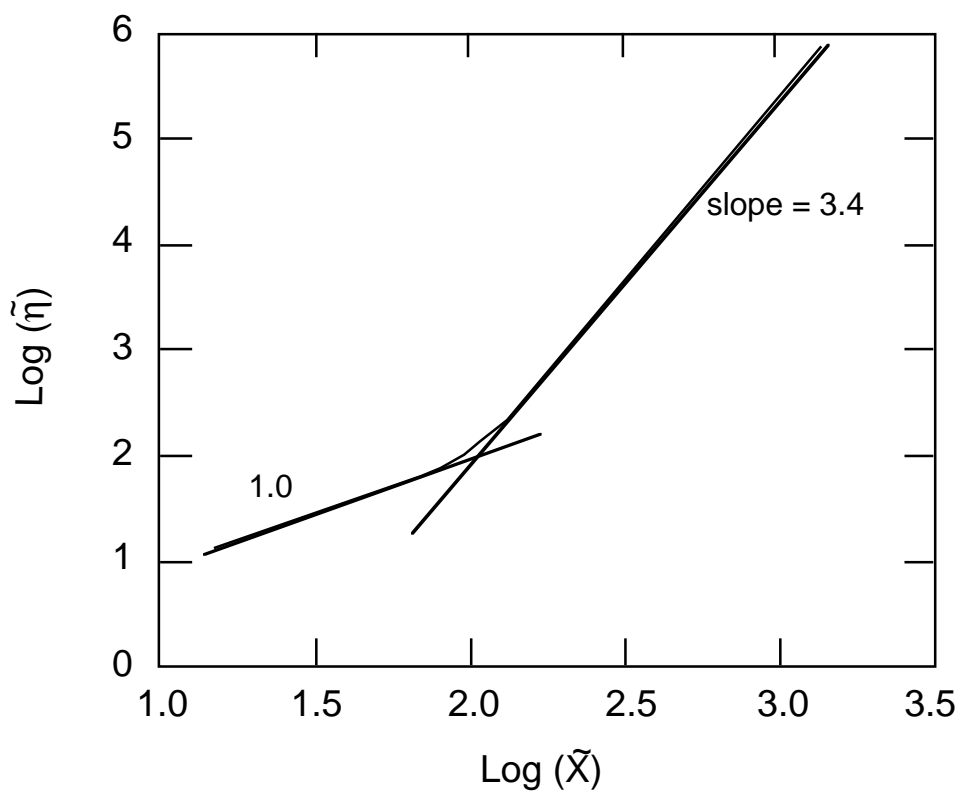
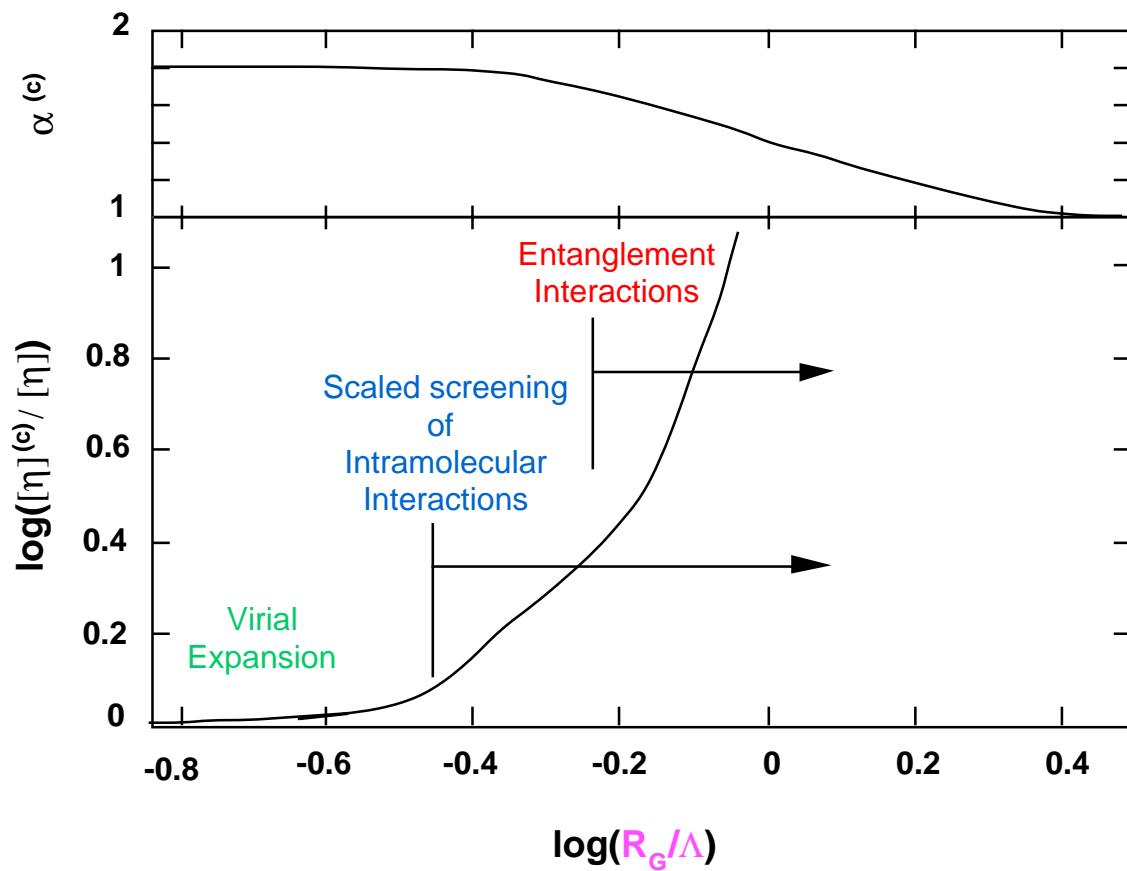
$\tilde{X}_c = \text{constant} \approx 100$; empirical for many systems

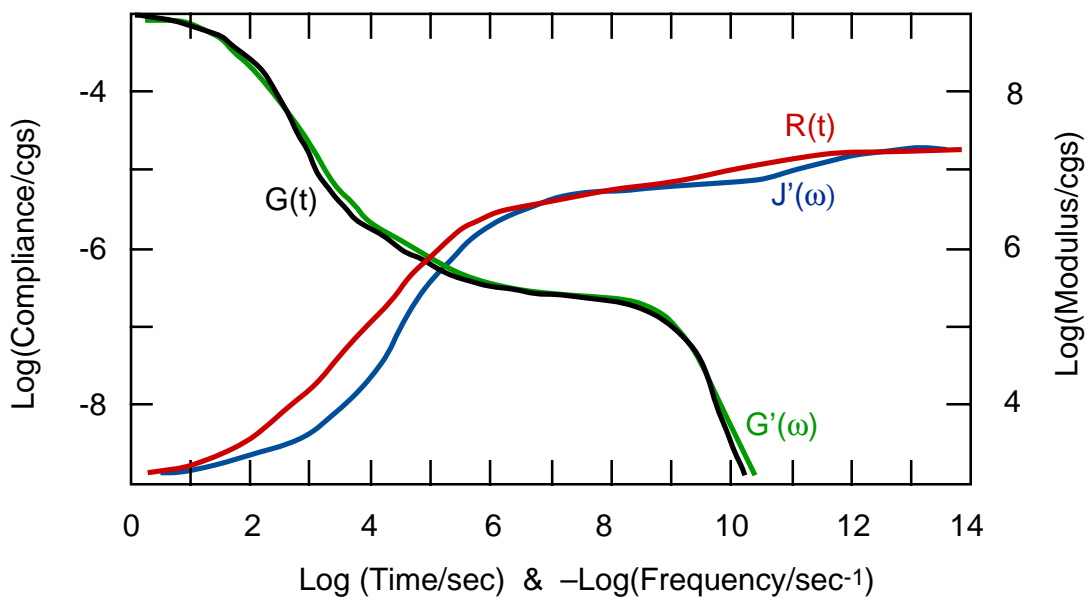
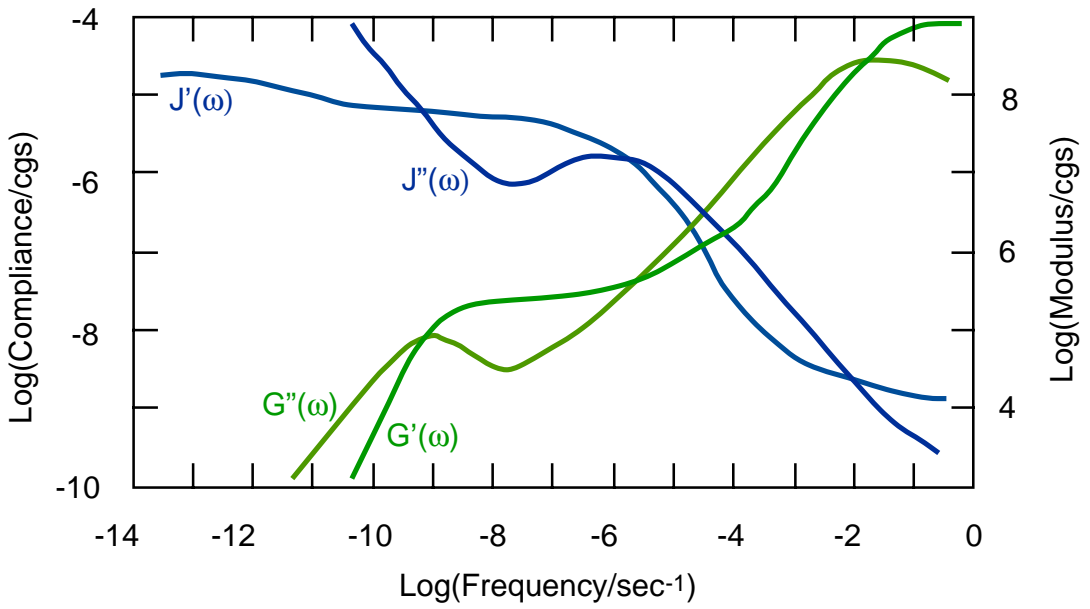
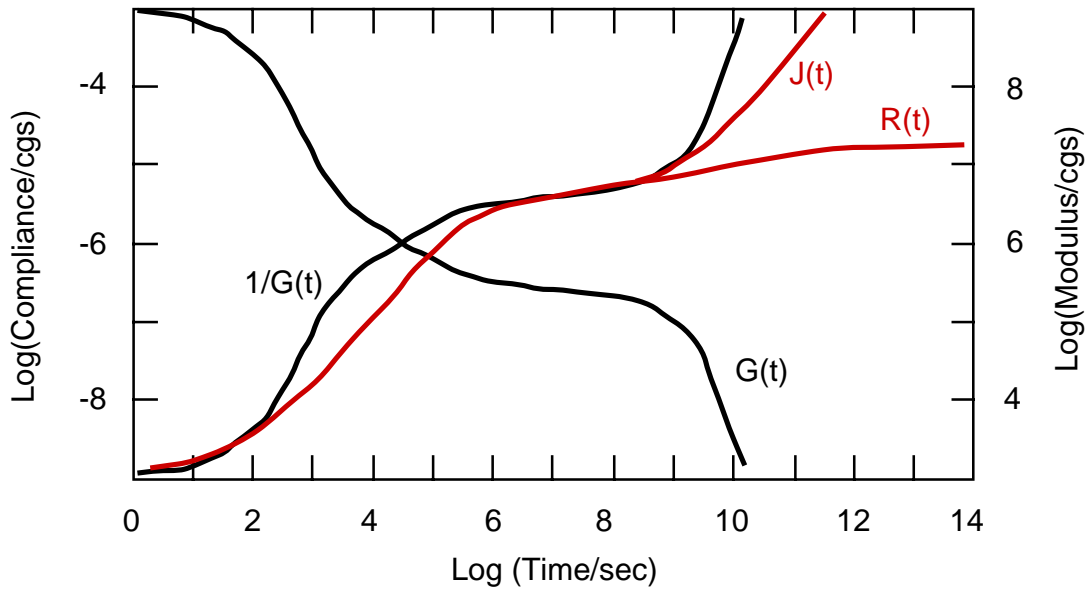
$$E(y) = \{1 + y^{4.8}\}^{1/2}$$

$$= [\eta]^{(c)}_{LOC} \{1 + c[\eta]^{(c)}\}$$

For a polydispersed linear polymer, use M_w to compute \tilde{X}

No single reduced concentration may be used to scale the reduced viscosity over the entire concentration range of interest.





The Steady-State Recoverable Compliance:

- For polymers and their concentrated solutions with $M < M_e$:

$$\diamond \quad J_S = J_{\text{Rouse}} = 2M/5RTc = 2M/5RT\rho\phi; \text{ "Rouse Behavior"}$$

- For polymers and their concentrated solutions with $M \gg M_e$:

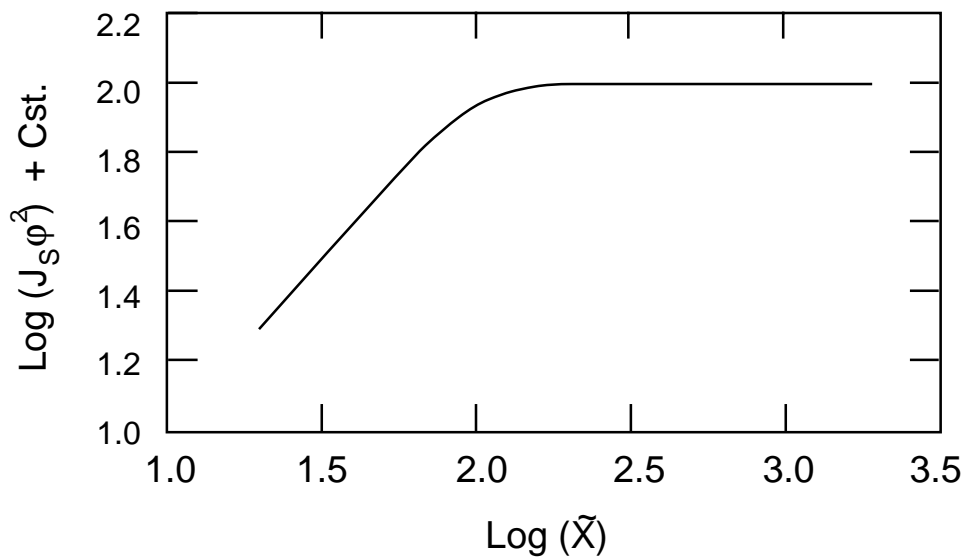
$$\diamond \quad J_S \approx kJ_N; \quad (k \approx 2-3 \text{ for a Narrow MWD})$$

$$J_N = 1/G_N = M_e/RT\rho\phi^2; \text{ Pseudo network compliance}$$

- Approximate "Cross-over" Expression:

$$\diamond \quad J_S = \{ (J_{\text{Rouse}})^{-\epsilon} + (kJ_N)^{-\epsilon} \}^{-1/\epsilon}$$

$$\diamond \quad J_S\phi^2 = (\phi M/\rho RT) \{ 1 + (\phi M/k^*M_e)^{\epsilon} \}^{-1/\epsilon}; \quad k^* \approx 4-6$$



Retardation and Relaxation Spectra

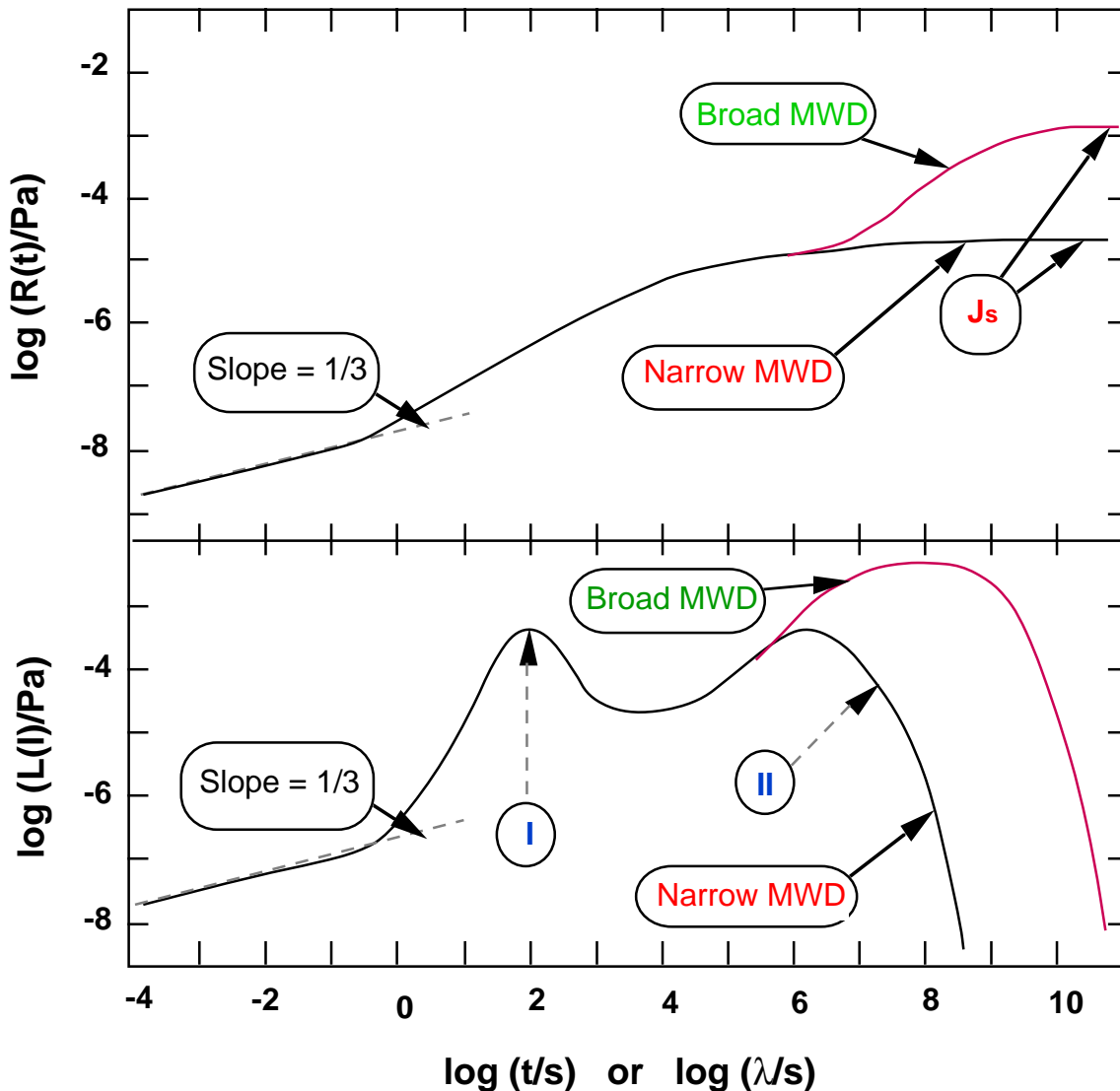
Retardation spectrum: $L(\lambda)$ with retardation times λ

Relaxation spectrum: $H(\tau)$ with relaxation times τ

Defining Functions:

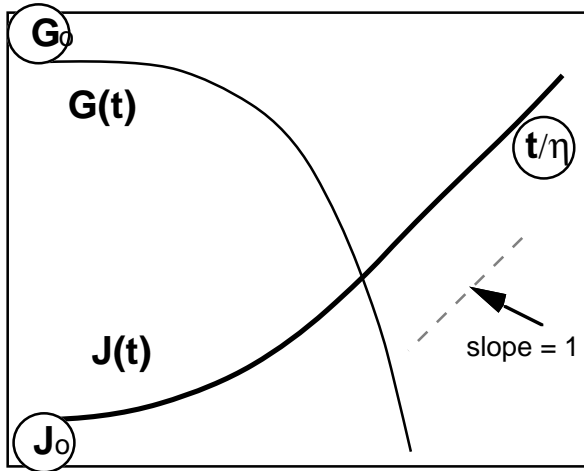
$$J(t) = J_s - [J_s - J_o]\alpha(t) + t/\eta$$
$$[J_s - J_o]\alpha(t) = \int_{-\infty}^{\infty} d(\ln \lambda) L(\lambda) \exp(-t/\lambda)$$

$$G(t) = G_e + [G_o - G_e]\varphi(t)$$
$$[G_o - G_e]\varphi(t) = \int_{-\infty}^{\infty} d(\ln \tau) H(\tau) \exp(-t/\tau)$$

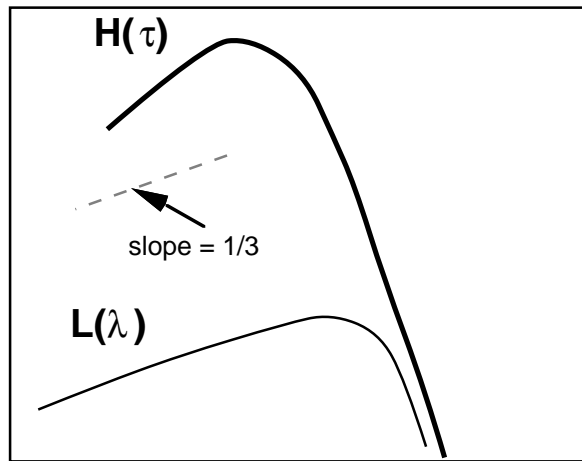


Remarks (Berry and Plazek, 1986):

- For crosslinked polymers, Peak II is absent, and Peak I represents the dynamics of chains between crosslink loci.
- For unentangled linear (or branched) polymers, Peak I increases with increasing cM_w , and Peak II is absent.
- For entangled linear (or branched) polymers, Peak I does not change with increasing M_w , and the retardation time λ_{max} for Peak II increases as $\lambda_{max} \propto (cM_w)^{3.4}$. Peak I reflects the dynamics of chains between crosslink loci in the entanglement pseudo-network, and Peak II reflects longer-range dynamics of the total chains (e.g., reptation-like dynamics).
- Example behavior is depicted schematically on the following page.

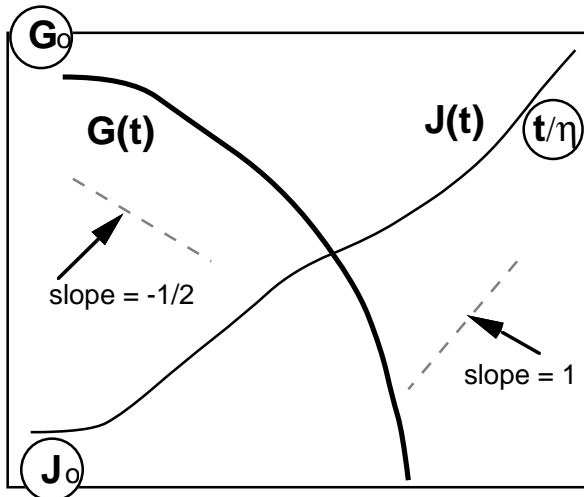


log t

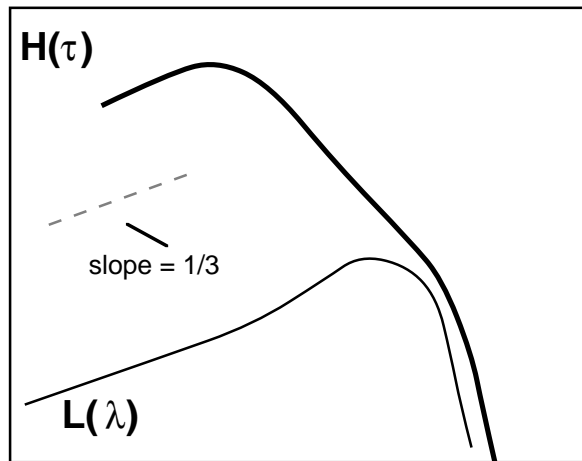


log λ or log τ

Low Molecular Weight Glass Former

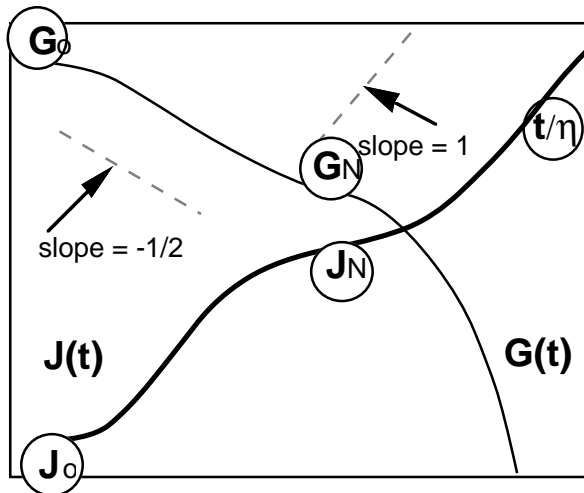


log t

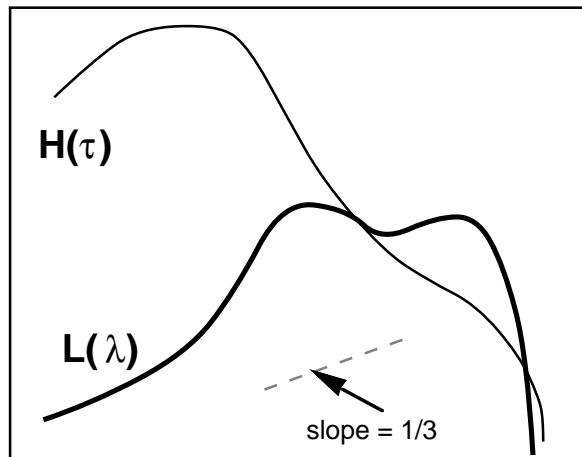


log λ or log τ

Polymeric Fluid with $M < M_e$



log t



log λ or log τ

Polymeric Fluid with $M \gg M_e$

THERMORHEOLOGICAL SIMPLICITY

- For a **Thermorheologically Simple** material, a "Time–Temperature" superposition obtains such that data over a range of temperature may be superposed on data at an arbitrary reference temperature T_{ref} by vertical and horizontal shifts $\log b$ and $\log a$, respectively, on bilogarithmic plots:

$\{J(t/a) - J_0\}/b$ and $b G(t/a)$ are found to be a functions of t/a , and otherwise independent of temperature.

$\{J'(a) - J_0'\}/b$ and $b G'(a)$ are found to be a functions of a , and otherwise independent of temperature.

$\{J''(a) - J_0''\}/b$ and $b G''(a)$ are found to be a functions of a , and otherwise independent of temperature.

$$b = J_s(T)/J_s(T_{ref})$$

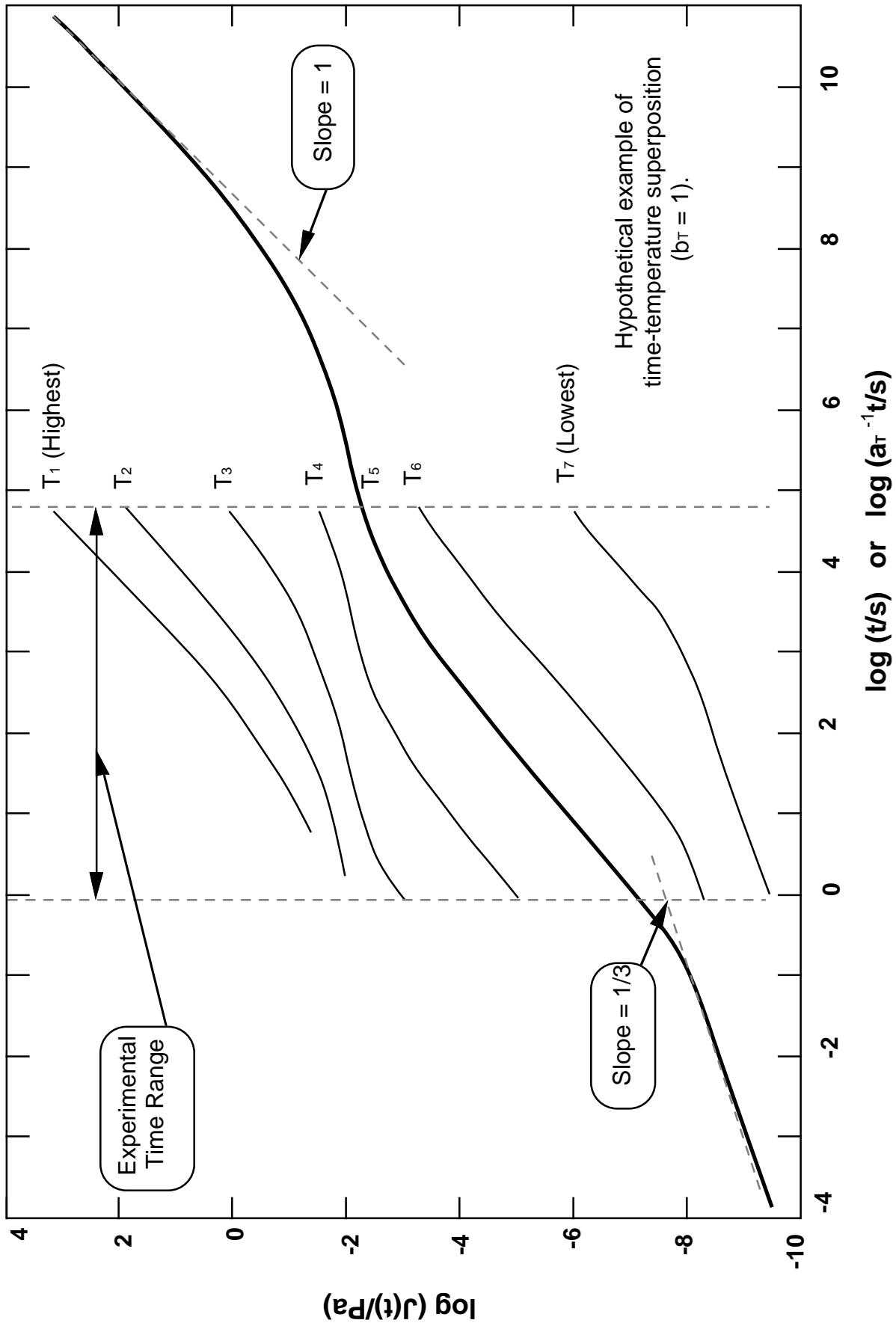
$$a = \tau_c(T)/\tau_c(T_{ref}) = b^{-1} \exp\left(\frac{K}{T - T_0}\right)$$

For many materials, the Vogel (or Vogel-Fulcher) relation obtains:

$$a = \exp\left(\frac{K}{T - T_0}\right) = \exp\left(\frac{K}{T - (T_g - \Delta T_g)}\right)$$

with $K \approx 2300K$ and $\Delta T_g \approx 60K$.

- Insofar as $b \gg 1$, thermorheological simplicity suggests that the viscoelastic functions will depend on the variables $t/\tau_c(T)$ and $\tau_c(T)$, and otherwise be independent of temperature, e.g., $J(t/\tau_c(T)) - R_0$ should be a function of $t/\tau_c(T)$, $J'(\tau_c(T)) - R_0$ should be a function of $\tau_c(T)$, etc.



ISOCHRONAL BEHAVIOR

- In some cases, the temperature is scanned while the dynamic properties are determined at fixed frequency; such experiments might typically be reported as $G'(\omega;T)$ and $\tan \delta(\omega; T)$ or $\eta'(\omega;T)$ versus T , depending on the application.
- Insofar as $G'(\omega\tau_c(T))$ and $G''(\omega\tau_c(T))$ as functions of $\omega\tau_c(T)$ are independent of T , the isochronal plots are seen to be mappings in which $\omega\tau_c(T)$ increases with decreasing temperature with:

$$\tau_c(T) \propto \exp\left(\frac{K}{T - (T_g - \Delta)}\right)$$

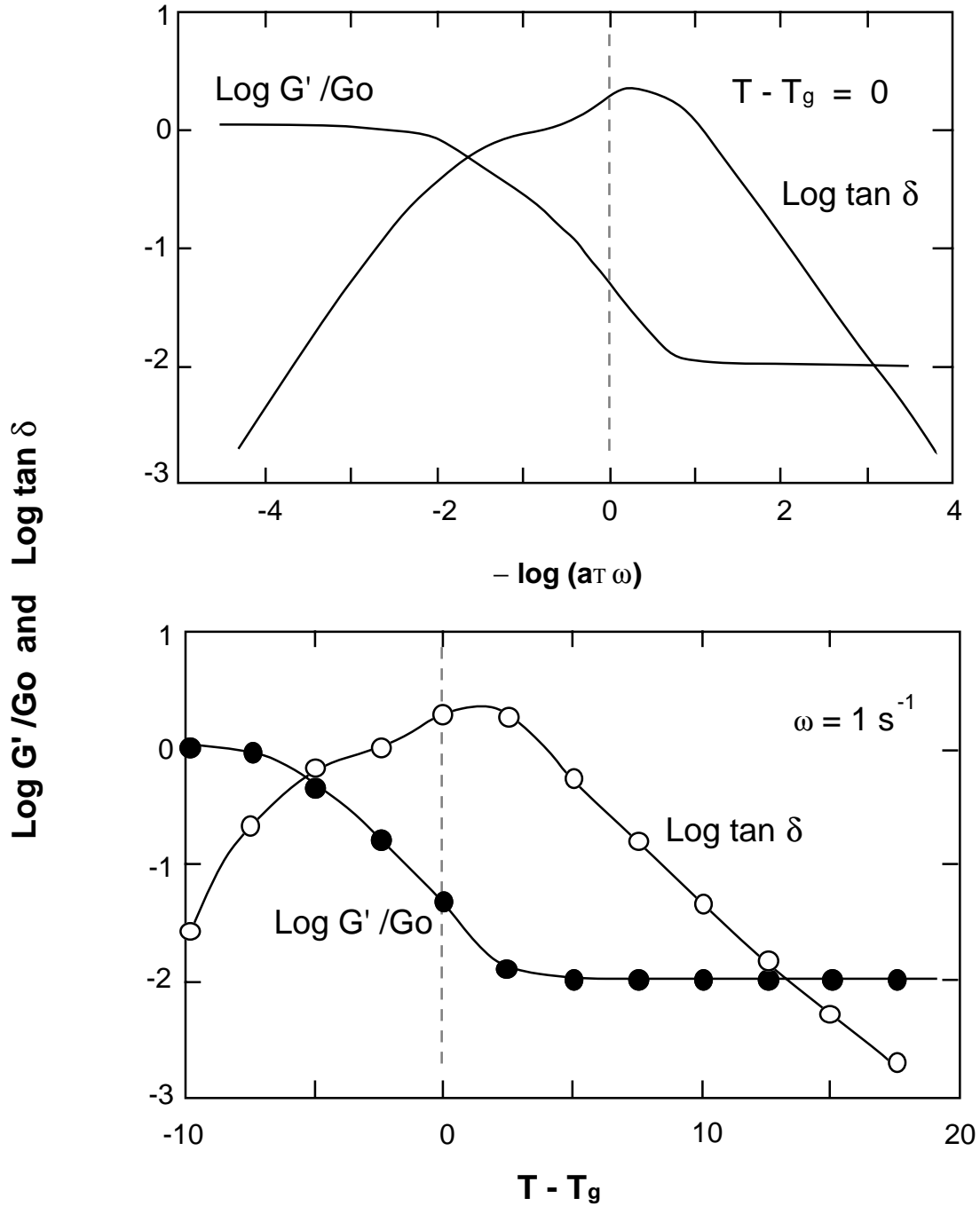
- For a reference temperature equal to the glass temperature T_g , so that $a_T = \tau_c(T)/\tau_c(T_g)$:

$$\ln a_T \omega = \ln \omega - \frac{K}{\Delta^2} \left(\frac{T - T_g}{1 + (T - T_g)\Delta} \right) \approx k_1 + k_2(T - T_g) + \dots$$

with the linear approximation valid for $(T - T_g) \ll \Delta$; $k_1 = \ln \omega$ and $k_2 = K/\Delta^2$.

- An example of $G'(\omega;T)$ and $\tan \delta(\omega; T)$ versus $\log(a_T\omega)$ and $T - T_g$ is given on the following page for a solid with $G_e/G_0 = 0.01$, and ten Rouse relaxation times, using the "universal" values $K = 2300$ K and $\Delta = 60$ K.

Example of $G'(\omega;T)$ and $\tan \delta(\omega;T)$ versus $-\log(a_T\omega)$ and $T - T_g$ for isothermal (upper) and isochronal (lower) experiments
 (See previous page)



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