

Translation - Rotation Paradox in Glass-forming Liquids

Slides for a lecture given by Frank H. Stillinger for a class in the Dept. of Chemistry of Princeton University

October 25, 2001

1. Self Diffusion "Constant"
 2. Velocity Autocorrelation Function
 3. Stokes-Einstein Hydrodynamic Approximation
 4. Test of Stokes-Einstein Relation for H₂O
 5. Rotational Diffusion
 6. Debye Model for Rotational Diffusion
 7. Test of Debye Approximation: H₂O Dielectric Relaxation Time*
 8. Shear Viscosity via Autocorrelation Functions
 9. Ortho-terphenyl (OTP)
 10. Heat capacity of *o*-terphenyl
 11. Log (Viscosity) vs. Reciprocal Temperature (°K)
 12. Resolution of Kohlrausch-Williams-Watts Relaxation Function
 13. Low-Temperature Translation-Rotation "Paradox"
 14. Experimental and Simulational Evidence for Dynamical Heterogeneity in Fragile Glasses
 15. Packing Views
 16. Crude Two-State Model to Rationalize the Translation-Rotation "Paradox"
 17. Numerical Values for Orthoterphenyl (OTP)
 18. Temperature - Dependent Absorption Maxima (Fragile Liquids)
 19. Structural Relaxation
 20. Research Problems
-

Self Diffusion "Constant"

- Fick's law for diffusion (macroscopic):

$$(\partial / \partial t)c(\mathbf{r}, t) = D\nabla^2 c(\mathbf{r}, t)$$

- $D(T, p)$ is the self-diffusion constant for a single-component medium, assumed to be at thermal ~~medium~~ *equilibrium*.

- Spatial broadening of an initially localized labeled sample:

$$c(\mathbf{r}, t) = (4\pi Dt)^{-3/2} \exp(-r^2 / 4Dt) \quad (\text{normalized}).$$

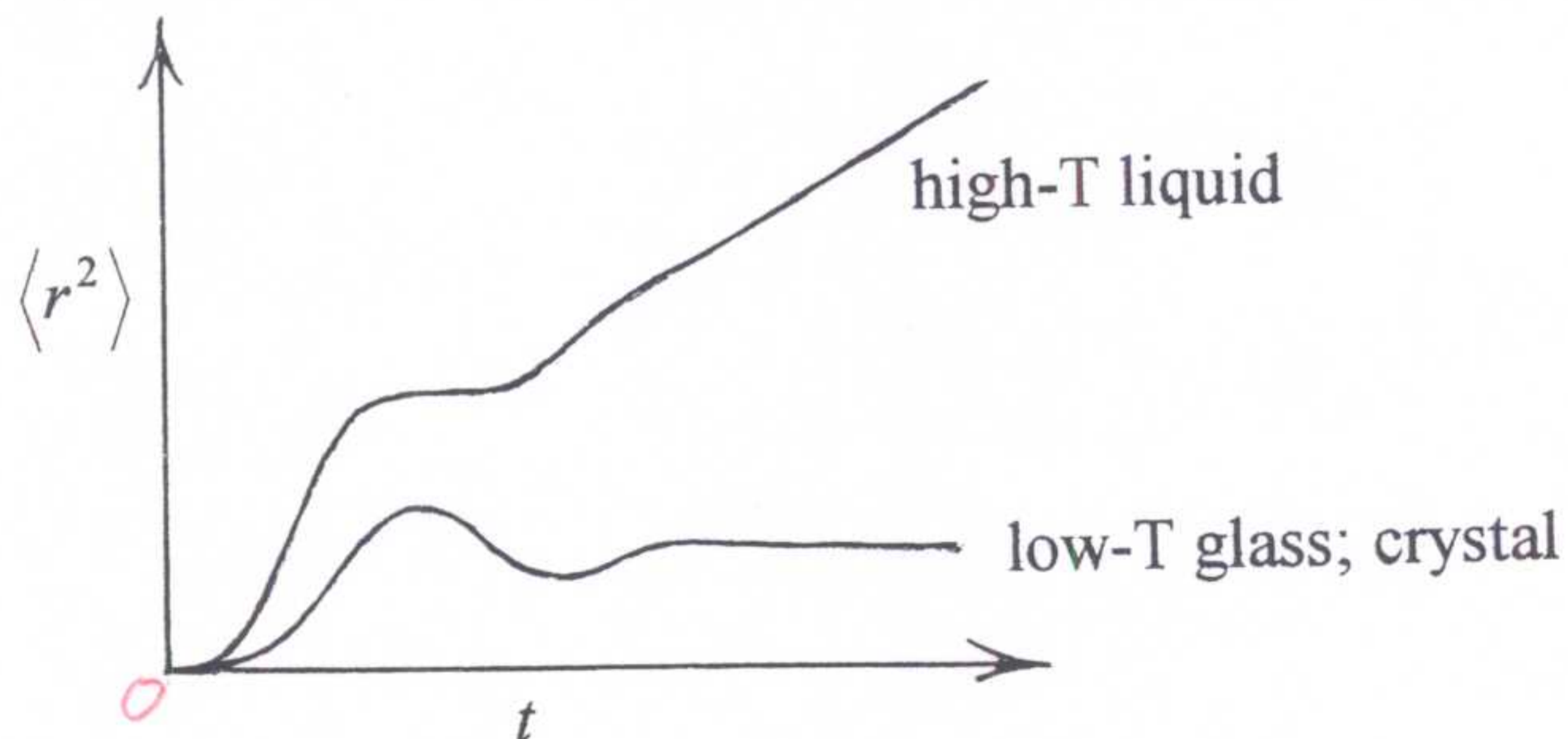
- Mean-square particle diffusive displacement:

$$\langle r^2 \rangle(t) = \int r^2 c(\mathbf{r}, t) d\mathbf{r} = 6Dt \quad ,$$

$$D = \frac{\langle r^2 \rangle(t)}{6t} \quad .$$

- Because this last expression emerges from a macroscopic law (Fick's), it refers only to times long on the molecular motion scale.

- Typical qualitative behaviors:



Velocity Autocorrelation Function

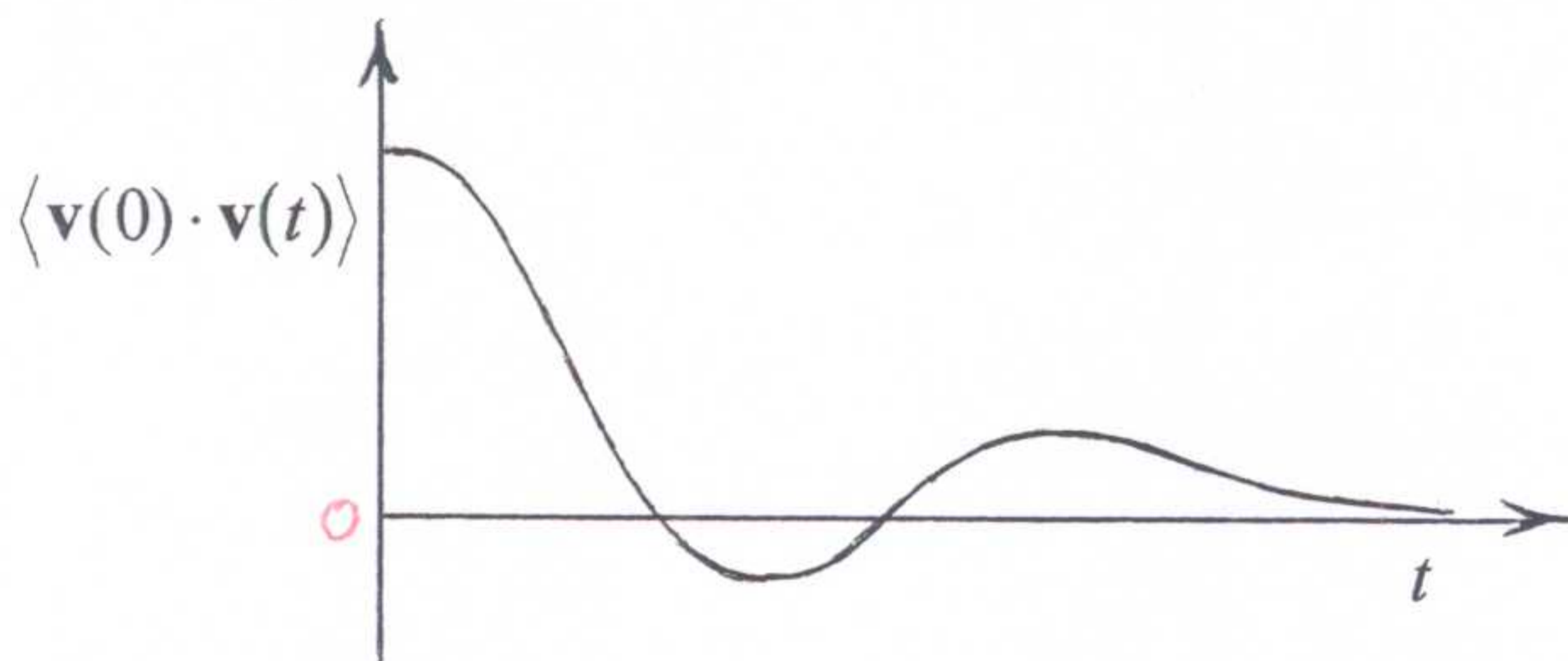
- Molecular displacement definition:

$$D = \lim_{t \rightarrow \infty} (6t)^{-1} \langle [\Delta \mathbf{r}_i(t)]^2 \rangle$$
$$= \lim_{t \rightarrow \infty} (6t)^{-1} \left\langle \int_0^t dt' \int_0^t dt'' \mathbf{v}_i(t') \cdot \mathbf{v}_i(t'') \right\rangle .$$

- $\langle \dots \rangle$ denotes equilibrium ensemble average.
- Evaluate limit to obtain D in terms of mean persistence of molecular velocity:

$$D = (1/3) \int_0^{\infty} \langle \mathbf{v}_i(0) \cdot \mathbf{v}_i(t) \rangle dt .$$

- Typical liquid-state pattern for velocity autocorrelation function, decaying to zero on the molecular time scale:



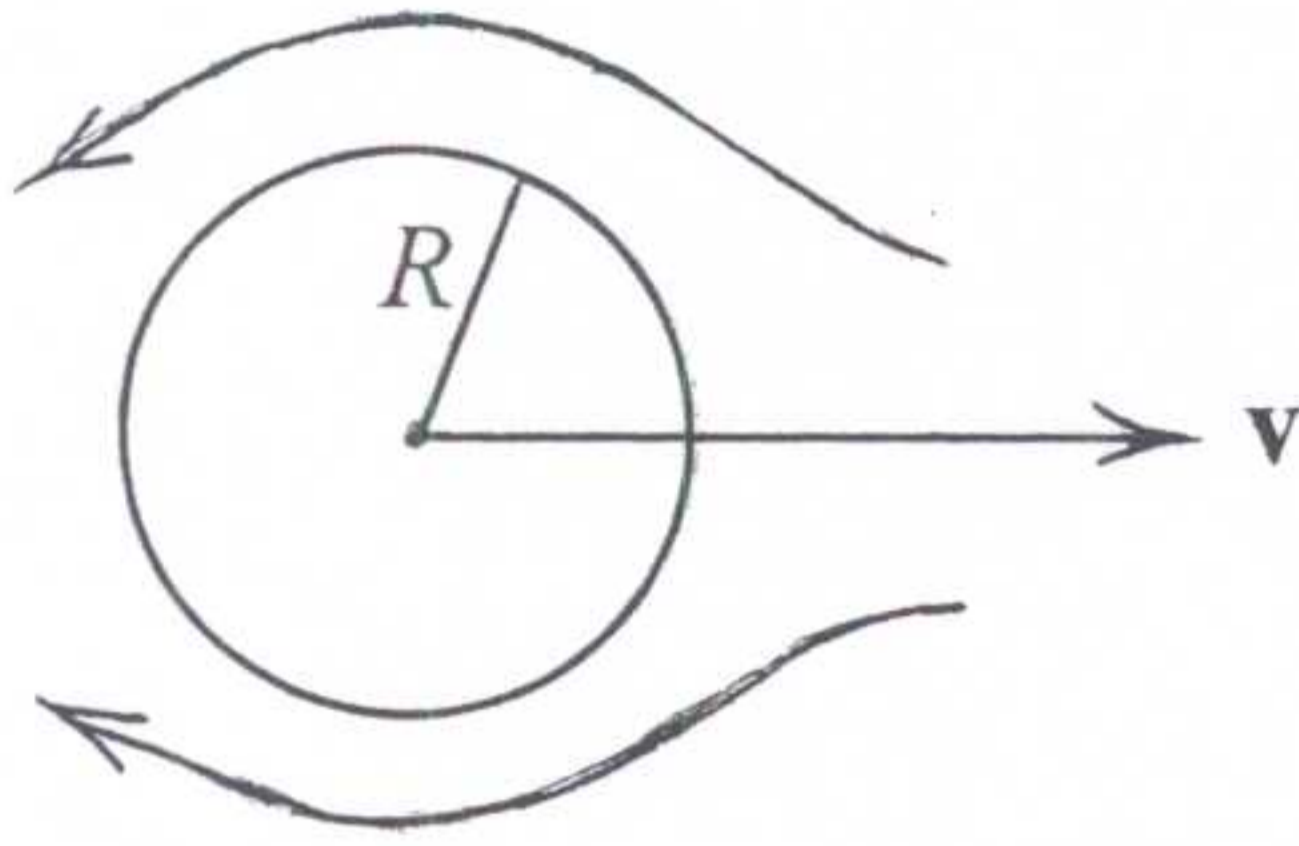
- Value at origin: $\langle \mathbf{v}_i(0) \cdot \mathbf{v}_i(0) \rangle = 3k_B T / m$.
- Note that different choices for “molecular center” are possible. This affects the velocity autocorrelation function, but not its integral.

Stokes-Einstein Hydrodynamic Approximation

- Linear frictional retardation for $t \geq 0$:

$$d\mathbf{v}(t) / dt \cong -\zeta\mathbf{v}(t) / m \quad (\zeta = \text{friction constant}) ,$$
$$\mathbf{v}(t) \cong \exp(-\zeta t / m)\mathbf{v}(0) .$$

- Hydrodynamic model: Radius- R sphere in viscosity- η incompressible fluid.



$$\zeta = C\pi R\eta ,$$
$$4(\text{slip}) \leq C \leq 6(\text{stick})$$

- Integrate velocity autocorrelation function expression to obtain:

$$D \cong \frac{k_B T}{\zeta} = \frac{k_B T}{C\pi R\eta(T)} .$$

- Experimental $D(T)$ data for equilibrium ($T \geq T_m$) and moderately supercooled liquids tends to track Stokes-Einstein predictions (with “reasonable” effective radii R).
- Obvious conceptual problems:
 - (a) Molecules not spherical (usually), not impenetrable (always).
 - (b) Local number density not constant [$g^{(2)}(r) \neq 1$].
 - (c) Ambiguous boundary condition.
 - (d) Apparent inconsistency of mixing discrete particle and continuum hydrodynamic descriptions.
 - (e) Hopping vs. smooth motion expected at low T .
 - (f) Wrong behavior predicted for dilute gas (vapor).

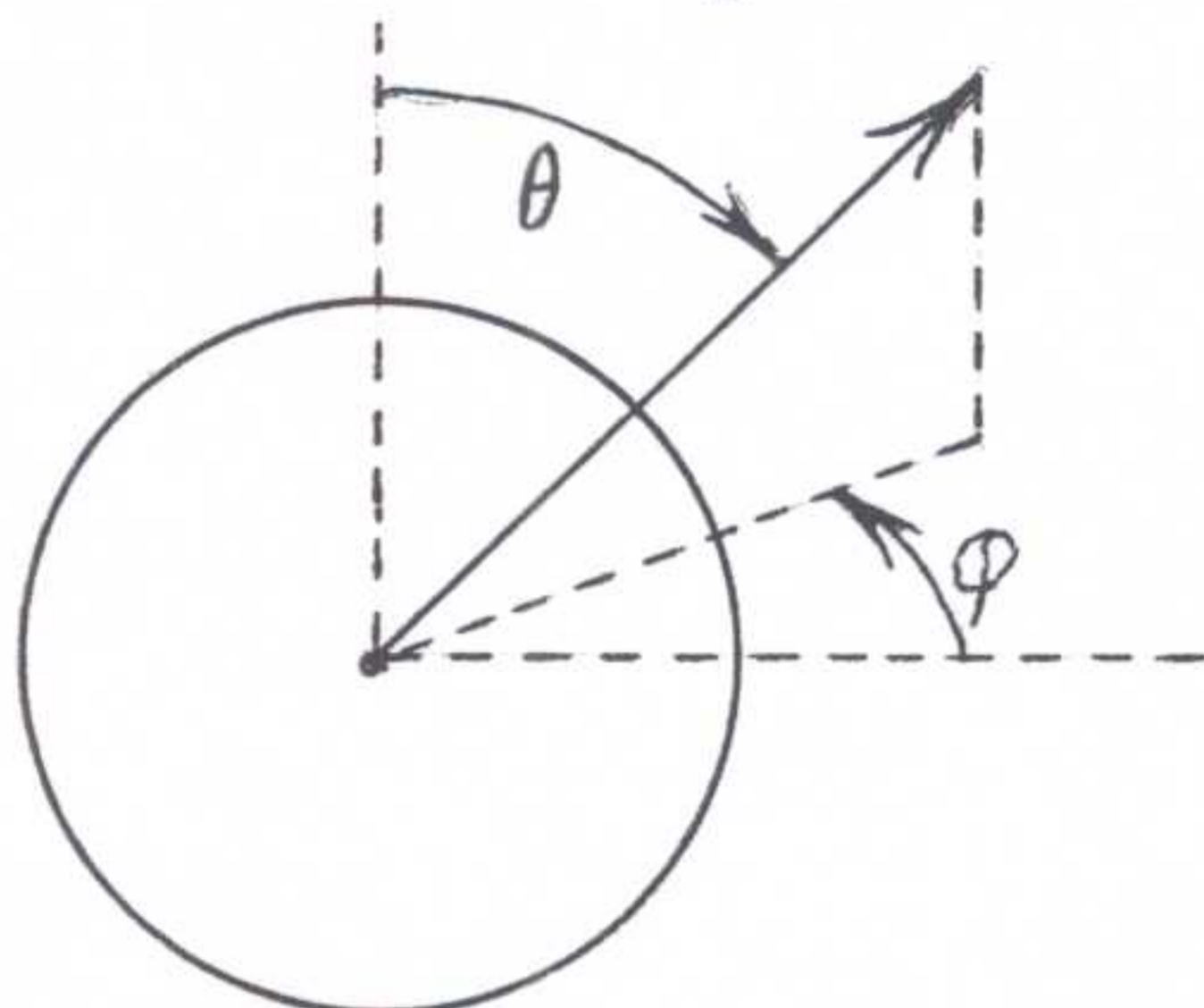
Test of Stokes-Einstein Relation for H₂O
(R=1.4 Angstroms)

T (K)	D (10 ⁻⁵ cm ² sec ⁻¹)*	η (cP)*	$C = \frac{k_B T}{\pi \eta D R}$
298.2	2.23	0.900	4.66
285.3	1.58	1.22	4.65
273.5	1.05	1.76	4.65
(T _m)			
263.7	0.700	2.53	4.67
261.5	0.633	2.85	4.55
258.7	0.553	3.26	4.50
255.8	0.477	3.74	4.50
254.0	0.438	4.15	4.39
251.8	0.395	4.67	4.28
250.0	0.341	5.33	4.32
248.2	0.321	6.45	3.76
246.3	0.263	7.32	4.02
244.4	0.219	8.82	3.97
242.5	0.187	10.8	3.77

* Data taken from: C.A. Angell, in F. Franks, *Water, A Comprehensive Treatise, Vol. 7* (Plenum Press, New York, 1982).

Rotational Diffusion

- Polar angles for reorienting molecule:



- Angular analog of Fick's law:

$$(\partial / \partial t) P(\theta, \varphi, t) = D_{rot} \nabla^2_{\theta, \varphi} P(\theta, \varphi, t) ,$$
$$\nabla^2_{\theta, \varphi} = \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \varphi^2} .$$

- Solution via spherical harmonics:

$$P(\theta, \varphi, t) = \sum_{l=0}^{\infty} \sum_{m=-l}^l A_{l,m} Y_{l,m}(\theta, \varphi) \exp(-t / \tau_l) ,$$
$$\tau_l = \frac{D_{rot}}{l(l+1)} .$$

- Analogous displacement relations:

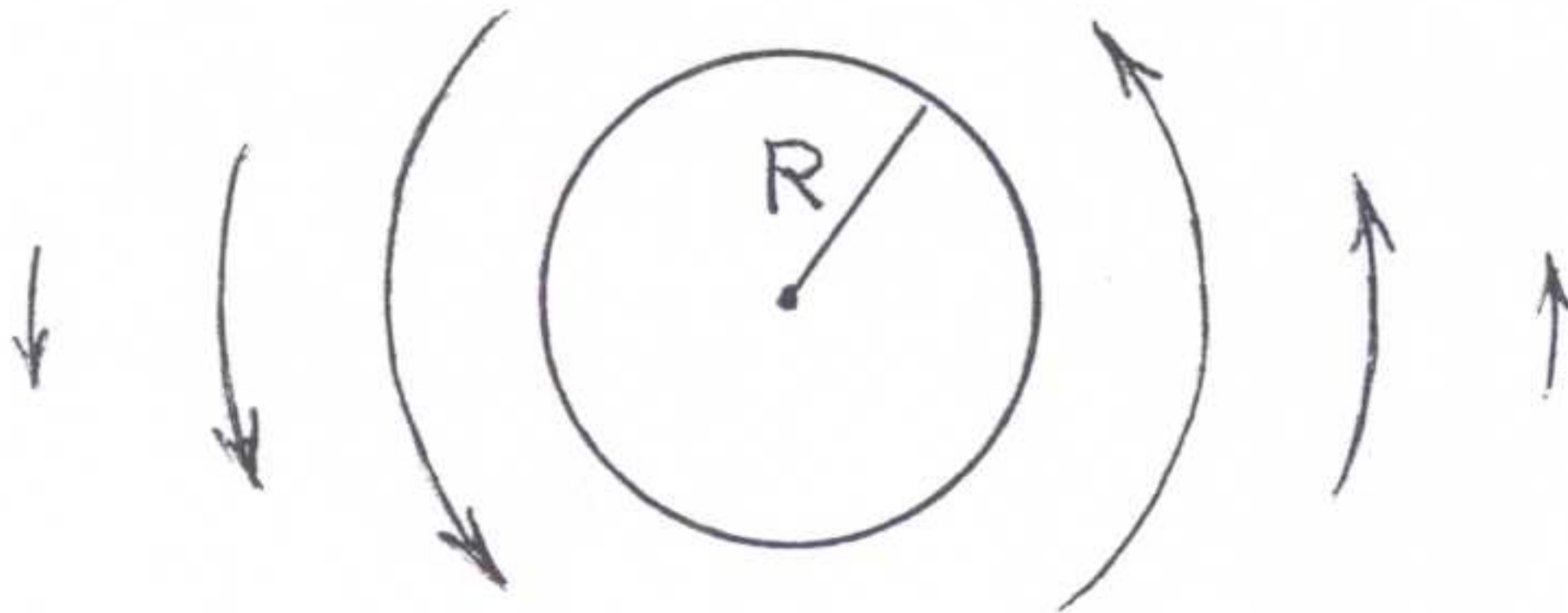
$$D_{trans} \cong \langle (\Delta \mathbf{r})^2 \rangle / 6 \Delta t ,$$
$$D_{rot} \cong \langle (\Delta \theta)^2 \rangle / 4 \Delta t .$$

Note difference in dimensions ($\text{cm}^2 \text{sec}^{-1}$ vs. sec^{-1}).

- Dielectric relaxation probes $l = 1$, nuclear magnetic resonance and depolarized Rayleigh scattering probe $l = 2$.

Debye Model for Rotational Diffusion

- Viscous damping of rotational motion for sphere:



- “Stick” boundary condition (“slip” is unphysical).
- Autocorrelation function of angular velocity ω :

$$D_{rot} \cong (1/2) \int_0^{\infty} \langle \omega(0) \cdot \omega(t) \rangle dt .$$

Note that this is only valid for strong damping due to finite extent of polar angle space.

- Debye model prediction (I =inertial moment of sphere):

$$\omega(t) = \omega(0) \exp[-(8\pi\eta R^3 / I)t] ,$$
$$D_{rot} = \frac{k_B T}{8\pi\eta R^3} .$$

- Same predicted T dependence as for Stokes-Einstein model of D_{rot} ,
namely $T / \eta(T)$. Trot
- Rotational relaxation time expressions:

$$\tau_l = \frac{8\pi\eta R^3}{l(l+1)k_B T} .$$

Test of Debye Approximation: H₂O Dielectric Relaxation Time*

$T(^{\circ}C)$	$\tau_{diel}(psec)$	$\eta(cP)$	$\frac{10^7 \tau_{diel} T}{\eta}$	$R(10^{-8} cm)^{**}$
0	17.7	1.787	2.71	1.44
10	12.6	1.306	2.73	1.44
20	9.5	1.002	2.78	1.45
30	7.4	0.798	2.81	1.45
40	5.9	0.653	2.83	1.46
50	4.8	0.547	2.84	1.46
60	4.0	0.467	2.85	1.46
75	3.2	0.379	2.84	1.48

* R.A. Robinson and R.H. Stokes, *Electrolyte Solutions* (Butterworths, London, 1968), p. 12, Table 1.1.

** $R = (k_B T \tau_{diel} / 4\pi\eta)^{1/3}$.

Shear Viscosity via Autocorrelation Functions

- Conventional expression involving persistence of shear stress:

$$\eta(T) = (k_B TV)^{-1} \int_0^{\infty} \langle J^{xy}(0) J^{xy}(t) \rangle dt ,$$

where J^{xy} is the x -direction flow of y -direction momentum:

$$J^{xy} = \sum_{j=1}^N (p_{jx} p_{jy} / m_j + x_j F_{jy}) .$$

This expression first appeared in: M.S. Green, J. Chem. Phys. **22**, 398 (1954).

- Unconventional expression involving persistence of shear flow:

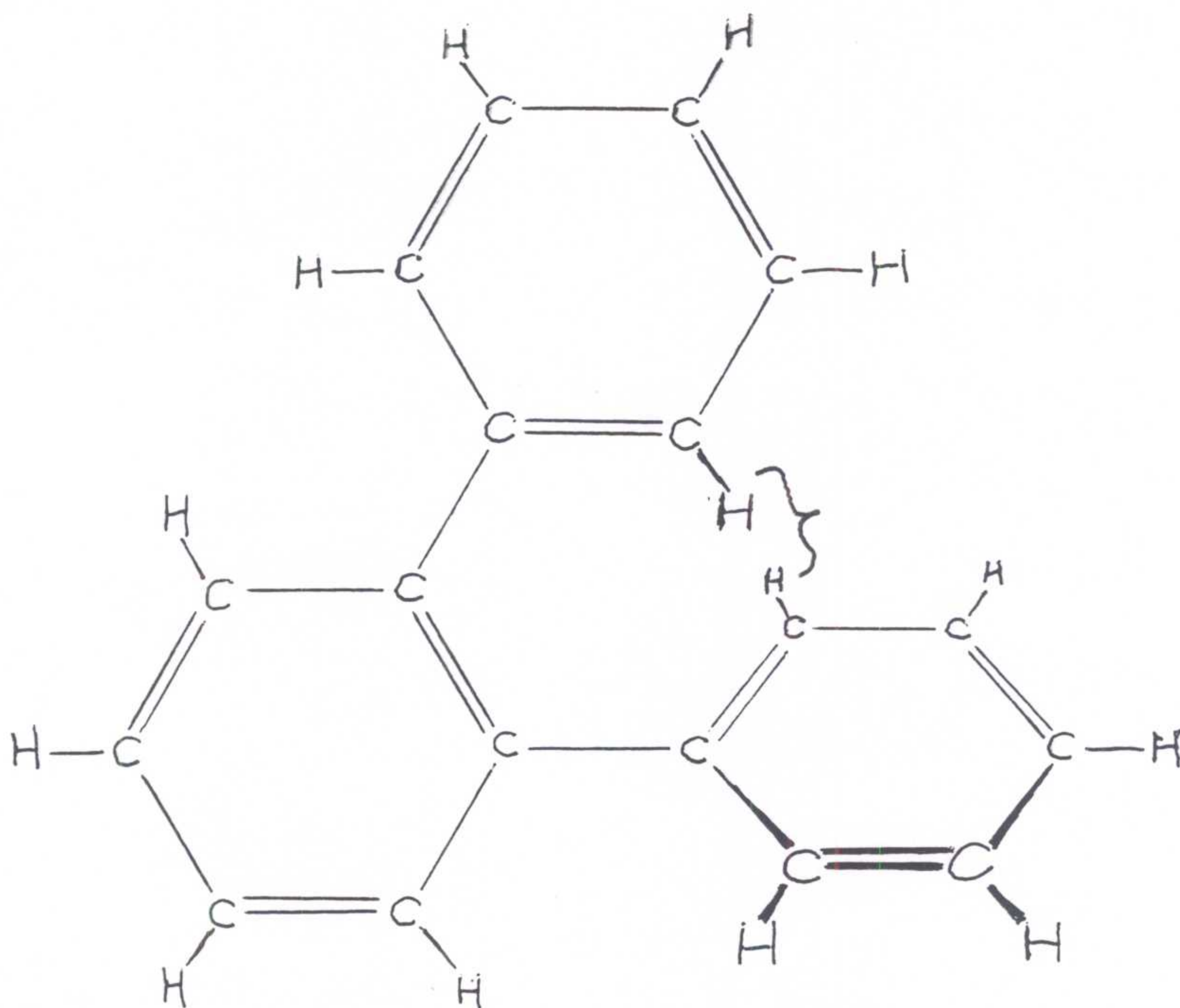
$$1 / \eta(T) = \lim_{q \rightarrow 0} (2Vq^2 / N^2 k_B T) \int_0^{\infty} \langle J_{xy}(0) J_{xy}(t) \rangle dt ,$$

where J_{xy} is the x -direction matter flow varying sinusoidally in the y direction:

$$J_{xy} = \sum_{j=1}^N (p_{jx} / m_j) \sin(qy_j) .$$

- • Supercooled liquid applications require restricting configuration space over which autocorrelation function averages are calculated.
- Positive, finite results from both expressions ultimately rely on the existence of fundamental transitions between steepest-descent basins for distinct inherent structures (local minima of the N -particle potential energy function).

ORTHO-TERPHENYL (OTP)
 $C_{18}H_{14}$



OTP: $T_g \cong 240\text{K}$

$T_K \cong 202.79\text{K}$

$T_M = 329\text{K}$

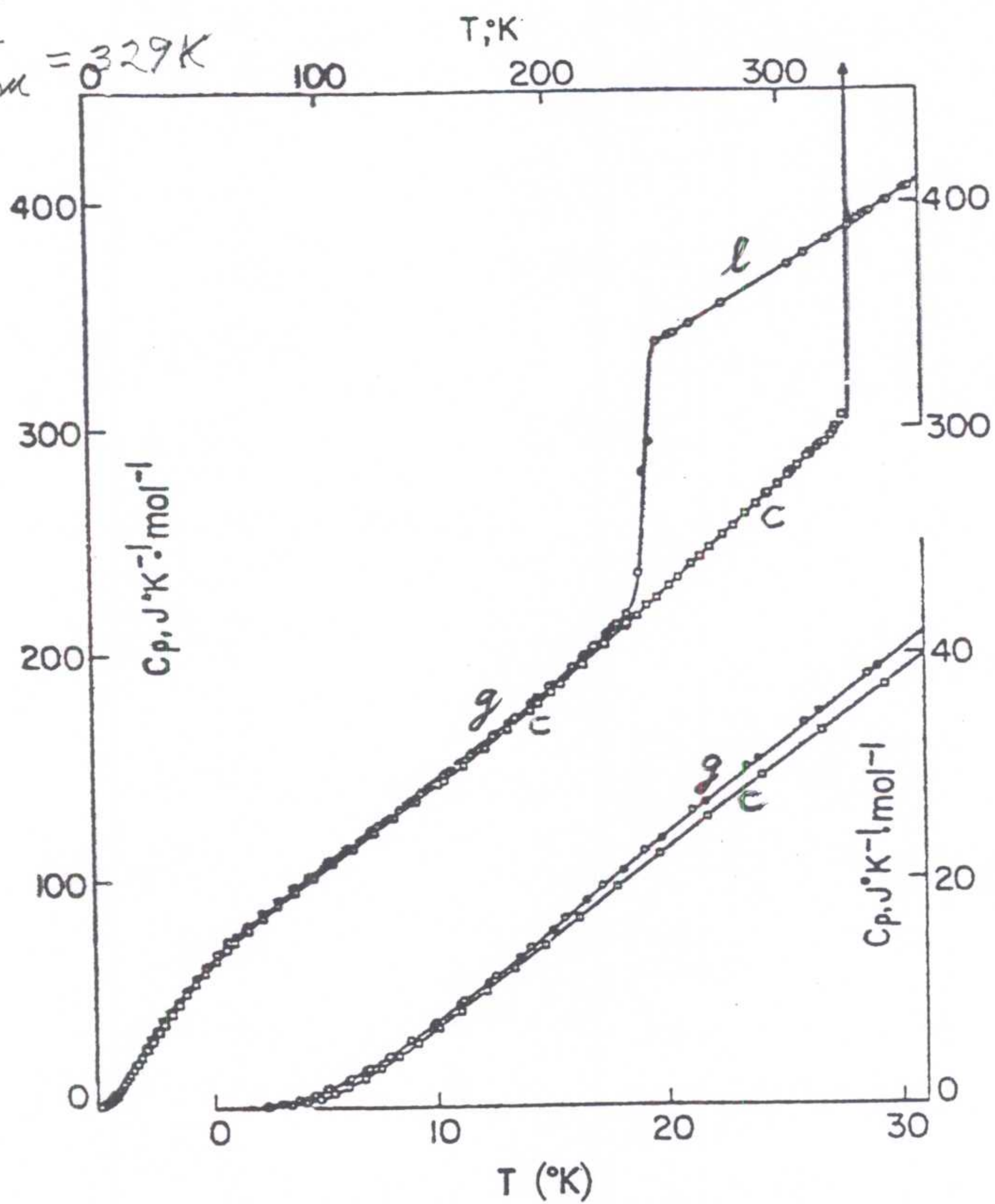
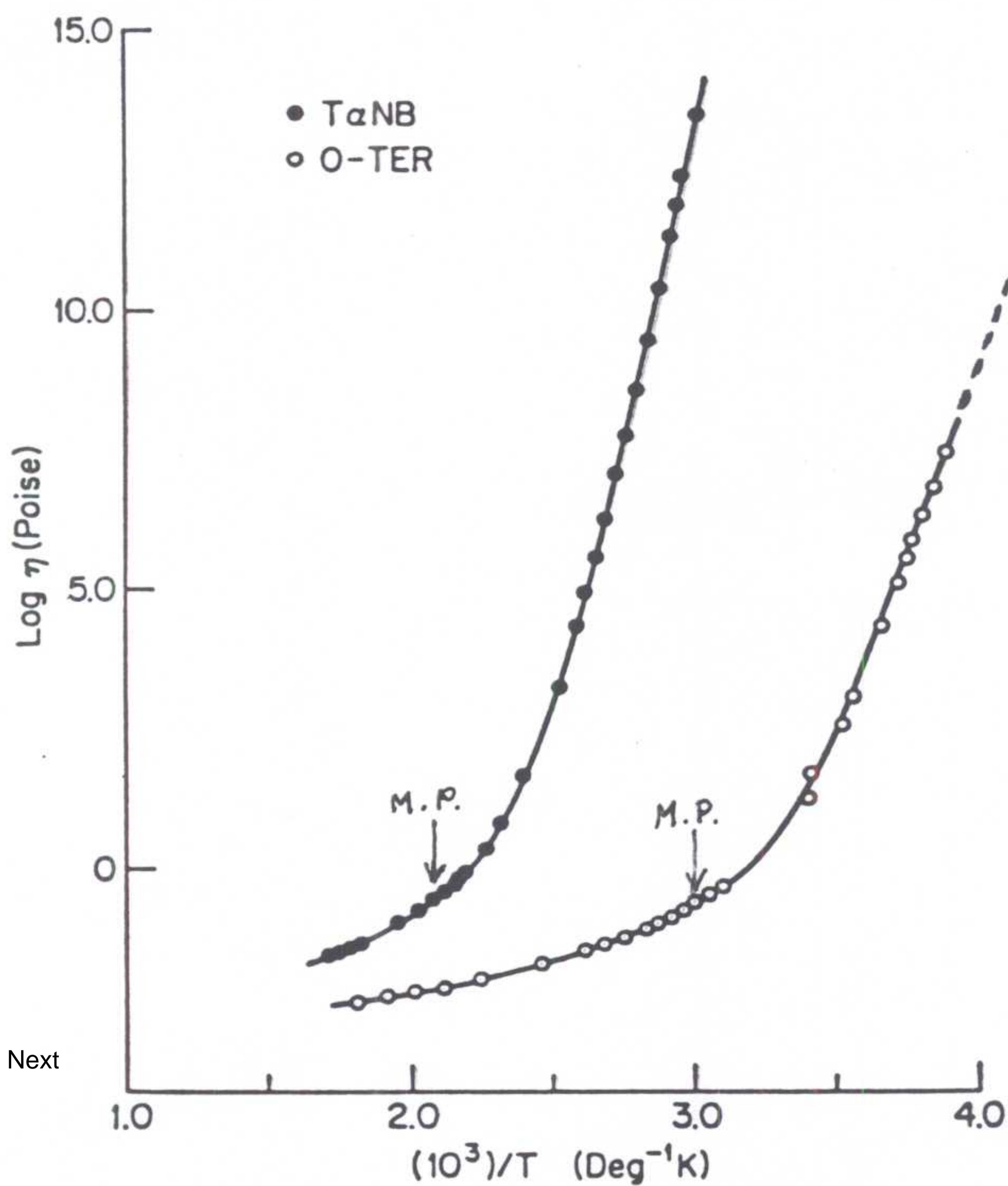


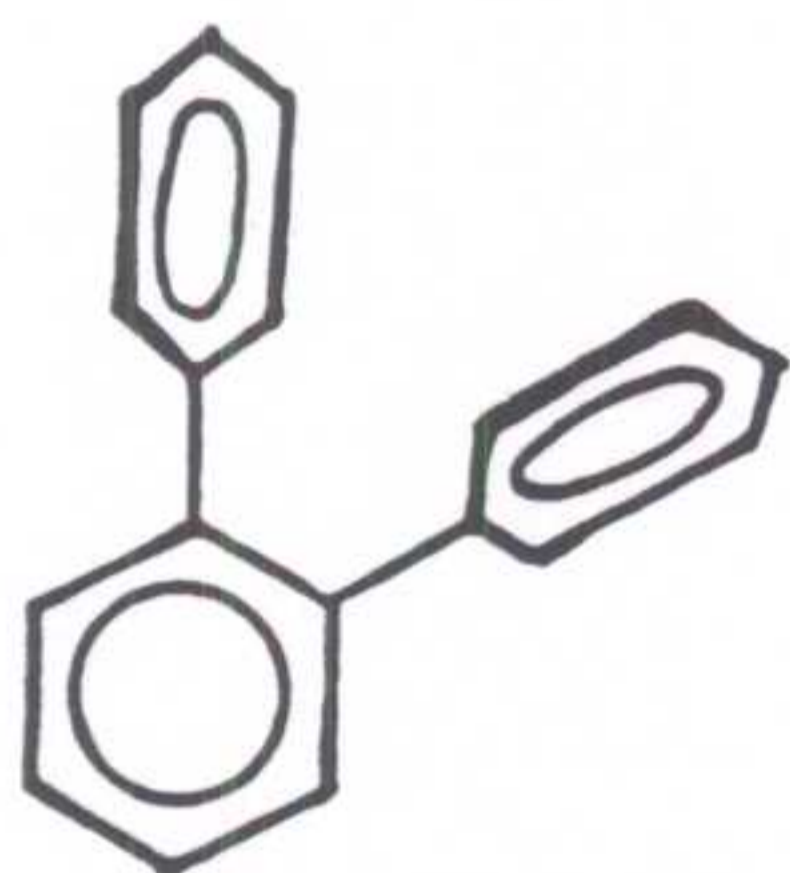
FIG. 1. Heat capacity of o-terphenyl: \square , crystal; \bullet , annealed glass; \circ , quenched glass and liquid.

[CHANG AND BESTUL, J. CHEM. PHYS. 56, 503 (1972)]

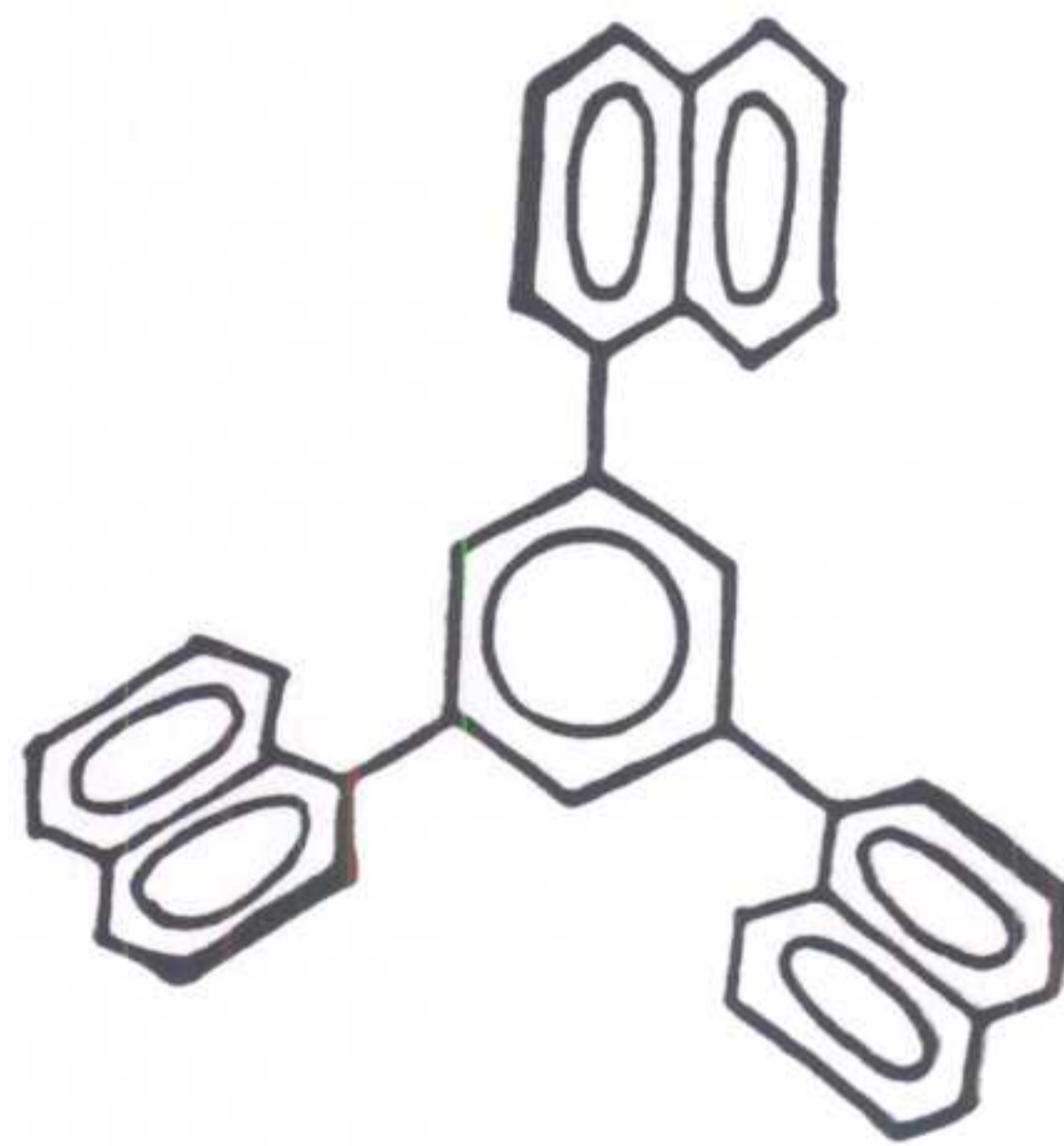


Frank H. Stilling
 Princeton University
 10-25-01
 Page 11 Previous Next
 Index

Figure 1. Log (viscosity) vs. reciprocal temperature (°K) for 1,3,5-tri- α -naphthylbenzene and α -terphenyl.



α -TERPHENYL



1,3,5-TRI- α -NAPHTHYL BENZENE

Resolution of Kohlrausch-Williams-Watts Relaxation Function

- “Stretched” exponential fit to experimental relaxation data (electrical, mechanical, thermal,):

$$f_{KWW}(t) = \exp[-(t / \tau_{KWW})^\beta] .$$

Applicable only for times long compared to molecular vibration periods.

- $\tau_{KWW}(T)$ roughly tracks $\eta(T)$ as $T \rightarrow T_g$ from above.
- Laplace transform resolves $f_{KWW}(t)$ into a linear superposition of simple exponentials ($W \geq 0$):

$$f_{KWW}(t) = \int_0^\infty W_\beta(\tau) \exp(-t / \tau) d\tau .$$

- As temperature decreases from $> T_m$ to $\approx T_g$, $\beta(T)$ decreases from ≈ 1 toward $\approx 1/3$ (but this is substance and property dependent).
- Decreasing β causes weight function $W(\tau)$ to broaden. Examples:

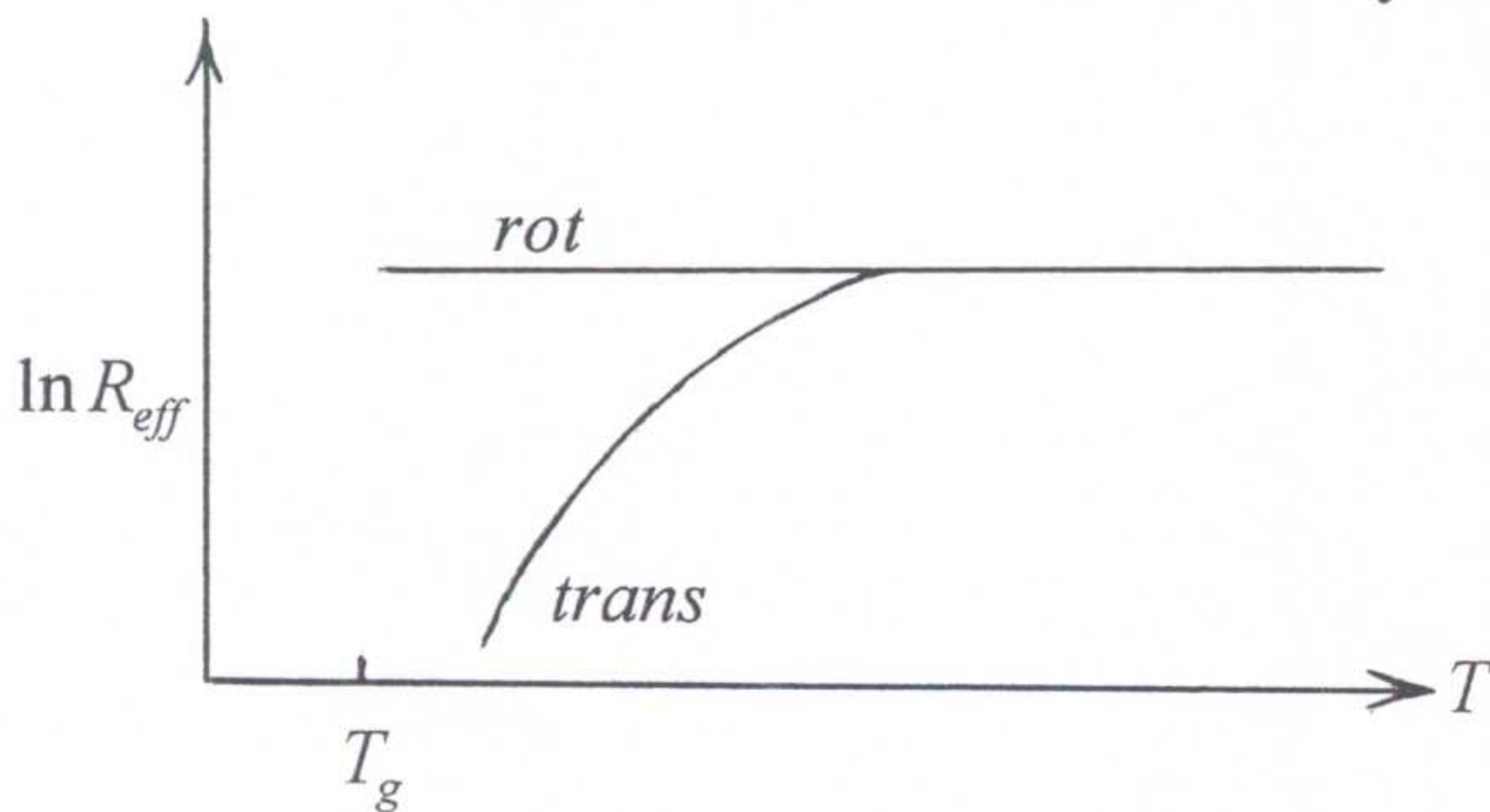
$$W_1(\tau) = \delta(\tau - \tau_{KWW}) ,$$
$$W_{1/2}(\tau) = \frac{\exp(-\tau / 4\tau_{KWW})}{2(\pi\tau_{KWW}\tau)^{1/2}} .$$

- Broadening of $W(\tau)$ can be reasonably interpreted as evidence for dynamic heterogeneity of highly viscous supercooled media. Each dynamical region has a simple exponential relaxation (approximately) with its own characteristic time scale for relaxation.

Caution: Boundaries and contents of dynamically distinct regions change with passage of time.

Low-Temperature Translation-Rotation “Paradox”

- Experimental observation: In fragile supercooled liquids approaching T_g , the temperature dependence of D_{rot} tracks $T / \eta(T)$, whereas D_{trans} declines far less rapidly with declining T .
- Thus rotational motion continues to adhere to the Debye model as $T \rightarrow T_g$, whereas translational motion departs from the analogous Stokes-Einstein model. This discrepancy is often referred to as the translation-rotation paradox.
- Representation in terms of an effective hydrodynamic radius:



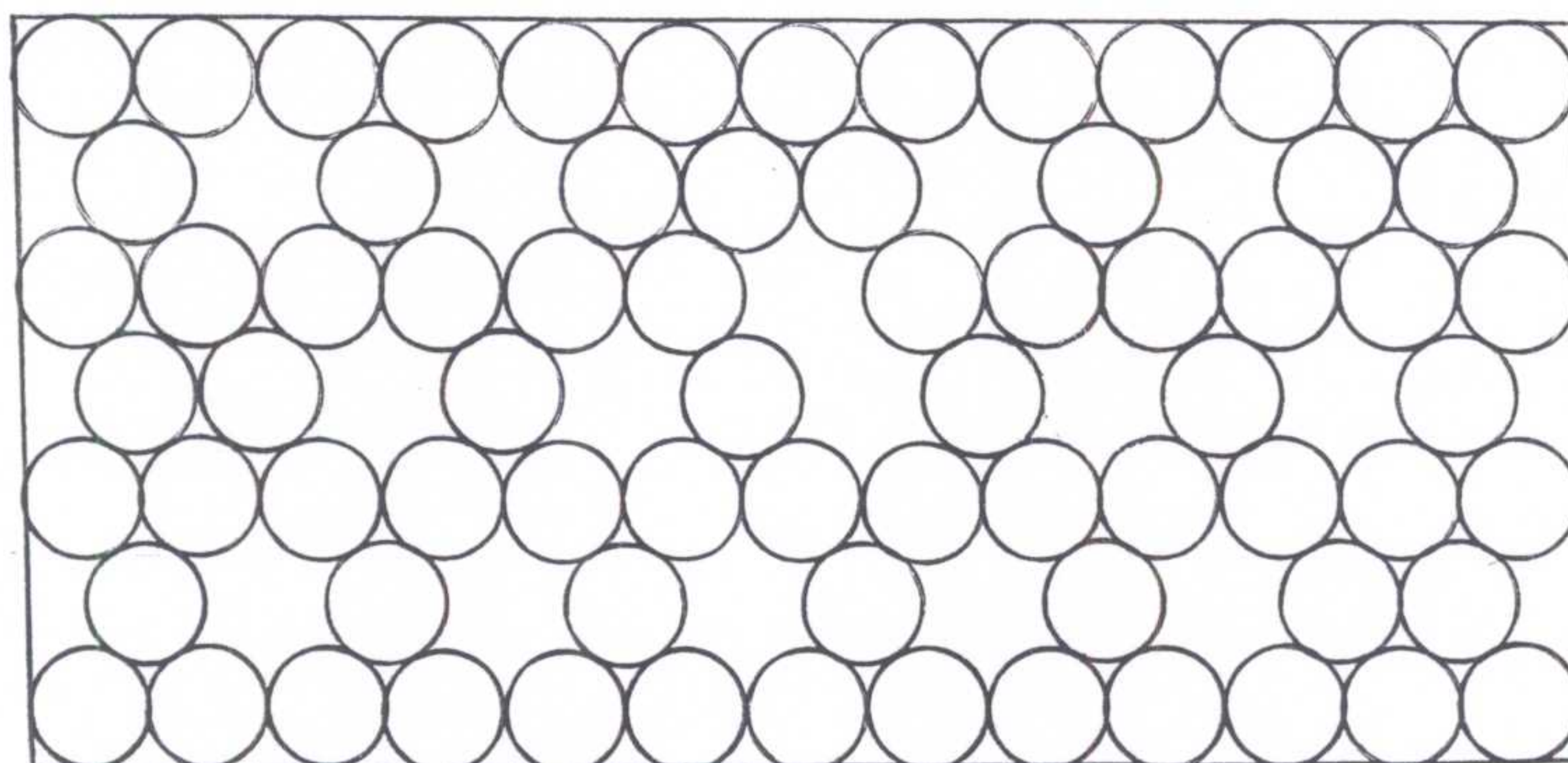
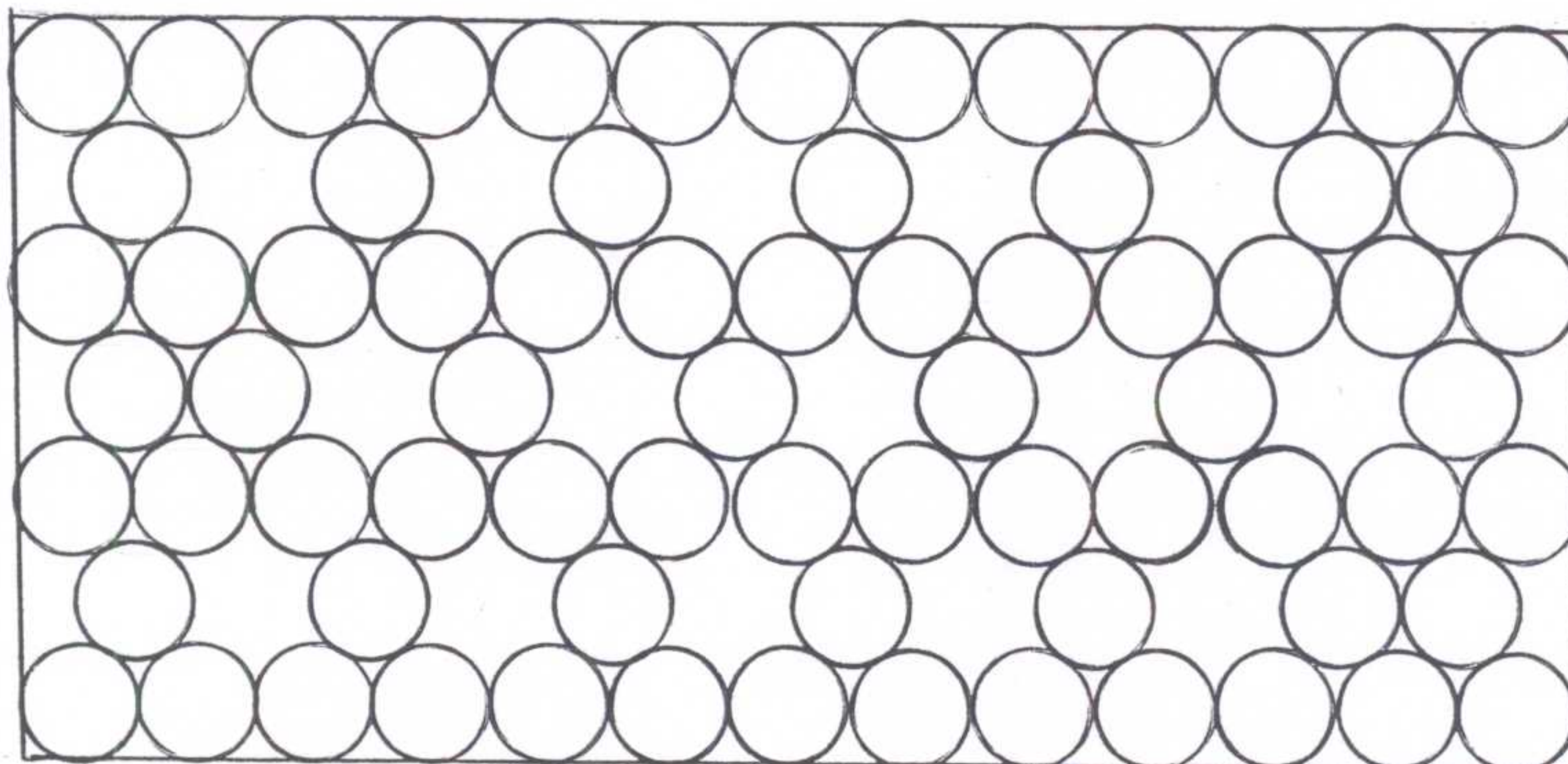
$(R_{eff})_{trans} / (R_{eff})_{rot} \rightarrow 10^{-2} - 10^{-3}$, but increases for large probes.

- References:
 - (1) G. Heuberger and H. Sillescu, J. Phys. Chem. **100**, 15255 (1996).
 - (2) F.R. Blackburn, C-Y. Wang, and M.D. Ediger, J. Phys. Chem. **100**, 18249 (1996).

**Experimental and Simulational Evidence
for Dynamical Heterogeneity in Fragile Glasses**

- (1) “Visualizing the collective motions responsible for the α and β relaxations in a model glass”, P. Harrowell, Phys. Rev. E **48**, 4359 (1993).
- (2) “Relaxation of spatially heterogeneous dynamic domains in supercooled ortho-terphenyl”, M.T. Cicerone and M.D. Ediger, J. Chem. Phys. **103**, 5684 (1995).
- (3) “Enhanced translation of probe molecules in supercooled o-terphenyl: Signature of spatially heterogeneous dynamics?”, M.T. Cicerone and M.D. Ediger, J. Chem. Phys. **104**, 7210 (1996).
- (4) “Dynamic heterogeneities in a supercooled Lennard-Jones liquid”, W. Kob, C. Donati, S.J. Plimpton, P.H. Poole, and S.C. Glotzer, Phys. Rev. Letters **79**, 2827 (1997).
- (5) “Spatially heterogeneous dynamics in supercooled liquids”, M.D. Ediger, Annu. Rev. Phys. Chem. **51**, 99 (2000).
- (6) “Chiral studies in amorphous solids: The effect of the polymeric glassy state on the racemization kinetics of bridged paddled binaphthyls”, J-W. Park, M.D. Ediger, and M.M. Green, J. Am. Chem. Soc. **123**, 49 (2001).
- (7) “Single molecule studies of heterogeneous dynamics in polymer melts near the glass transition”, L.A. Deschenes and D.A. Vanden Bout, Science **292**, 255 (2001).

PACKING VIEWS



Crude Two-State Model
to Rationalize the Translation-Rotation “Paradox”

- Divide the cold glass-forming medium into a dynamically inert major portion, and embedded ephemeral “fluidized” domains:



- Diffusion, relaxation processes dominated by fluidized-domain molecular motions.
- Four temperature-dependent average domain characteristics:
 - (a) volume v_0 ; (b) internal viscosity η_0 ;
 - (c) appearance rate per unit volume r_0 ; (d) lifetime t_0 .
- Infrequent appearance of fluidized domains bottlenecks both rotational and translational diffusion. But large v_0 and t_0 would disproportionately compensate only translational bottlenecking. Only the early phase of t_0 contributes to rotational relaxation, but translational diffusion continues throughout t_0 .
- Macroscopic viscosity related to rate of local stress relief as domains spontaneously appear: $\eta \approx (r_0 v_0)^{-1}$.

- Diffusion constant expressions:

$$D_{trans} \approx \frac{k_B T r_0 v_0 t_0}{6\pi\eta_0 R} , \quad D_{rot} \approx r_0 v_0 / 2 .$$

- Inequalities required for “paradoxical” D_{trans}, D_{rot} behavior:

$$\frac{4\pi\eta_0 R^3}{k_B T} \ll t_0 \ll \frac{\pi\eta_0 v_0^{2/3} R}{k_B T} .$$

Numerical Values for Orthoterphenyl (OTP)

[F.H. Stillinger and J.A. Hodgdon, J. Chem. Phys. **50**, 2064 (1994);
53, 2995 (1996).]

- Measured properties:

$T_m(K)$	329
$T_g(K)$	240
$\eta(T_m)(P)$	0.37
$\eta(T_g)(P)$	4×10^{12}
$\rho(T_g)(A^{-3})$	2.94×10^{-3}
$R(A)$	≈ 3.5

- Alternative parameter selections to produce enhancement of D_{trans} over the Stokes-Einstein prediction at T_g by factor 10^2 (D_{rot} remains unchanged from Debye form):

$v_0(A^3)$	3.40×10^6	1.70×10^5
$r_0(cm^{-3} sec^{-1})$	2.11×10^{13}	2.11×10^{15}
$t_0(sec)$	0.426	0.426
$\eta_0(P)$	1.22×10^6	6.10×10^6

Number of molecules per domain:

$$n_0 = \rho v_0 \quad 10^4 \quad 500$$

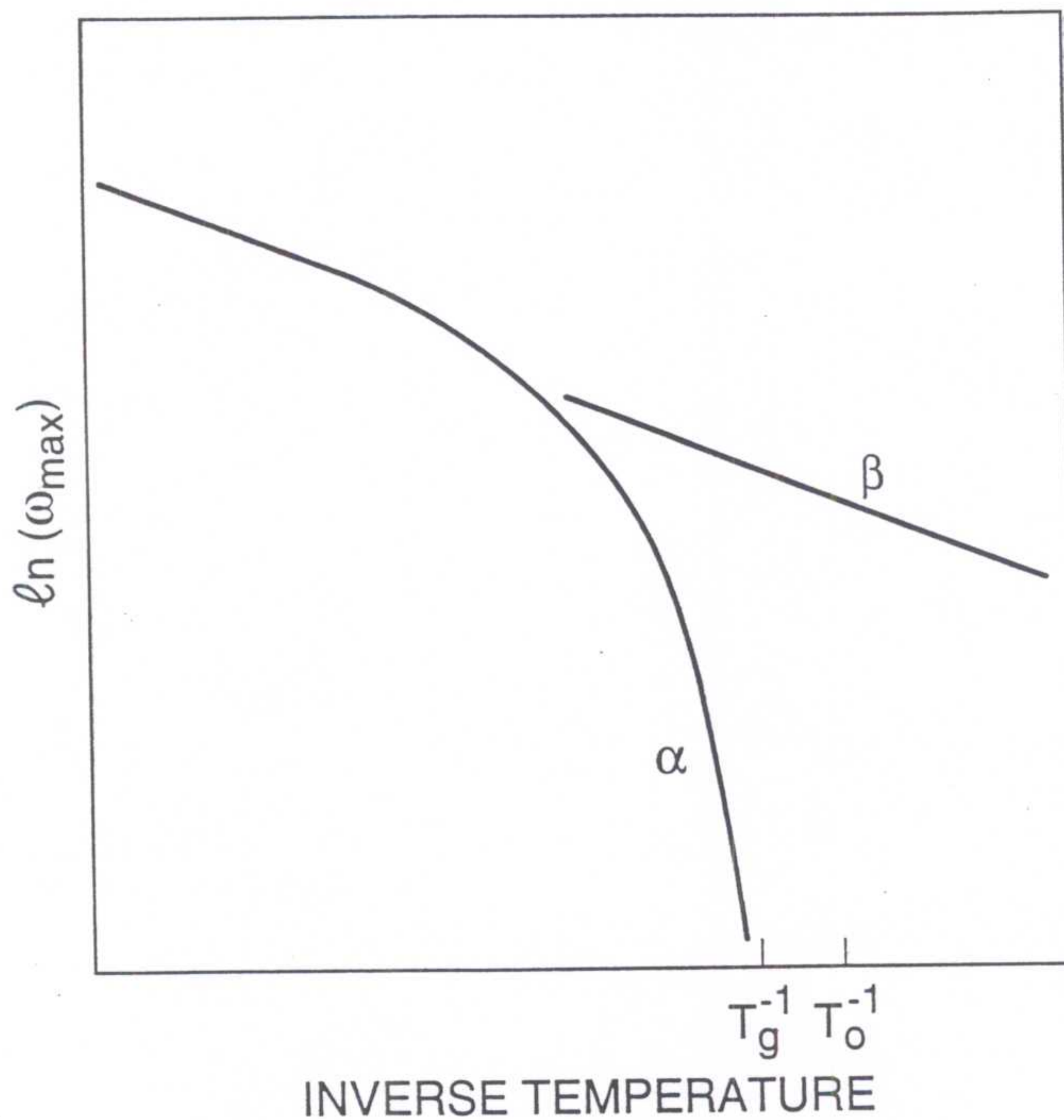
Concentration of domains:

$$c_0 = r_0 t_0 (cm^{-3}) \quad 8.99 \times 10^{12} \quad 8.99 \times 10^{14}$$

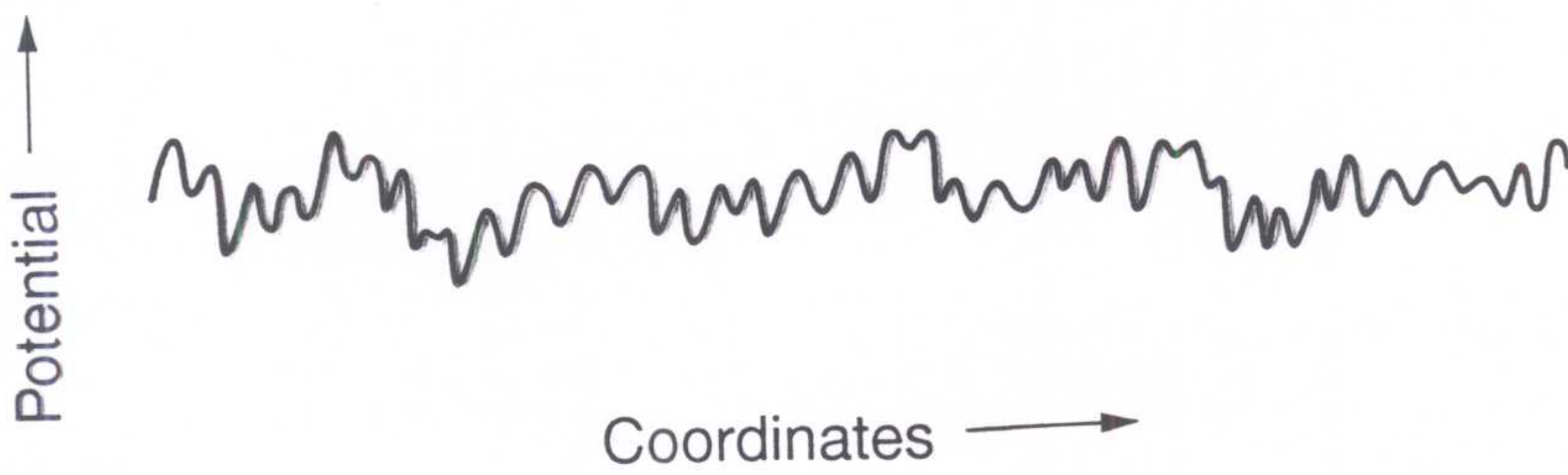
Volume fraction within domains:

$$\varphi_0 = r_0 t_0 v_0 \quad 3.06 \times 10^{-5} \quad 1.53 \times 10^{-4}$$

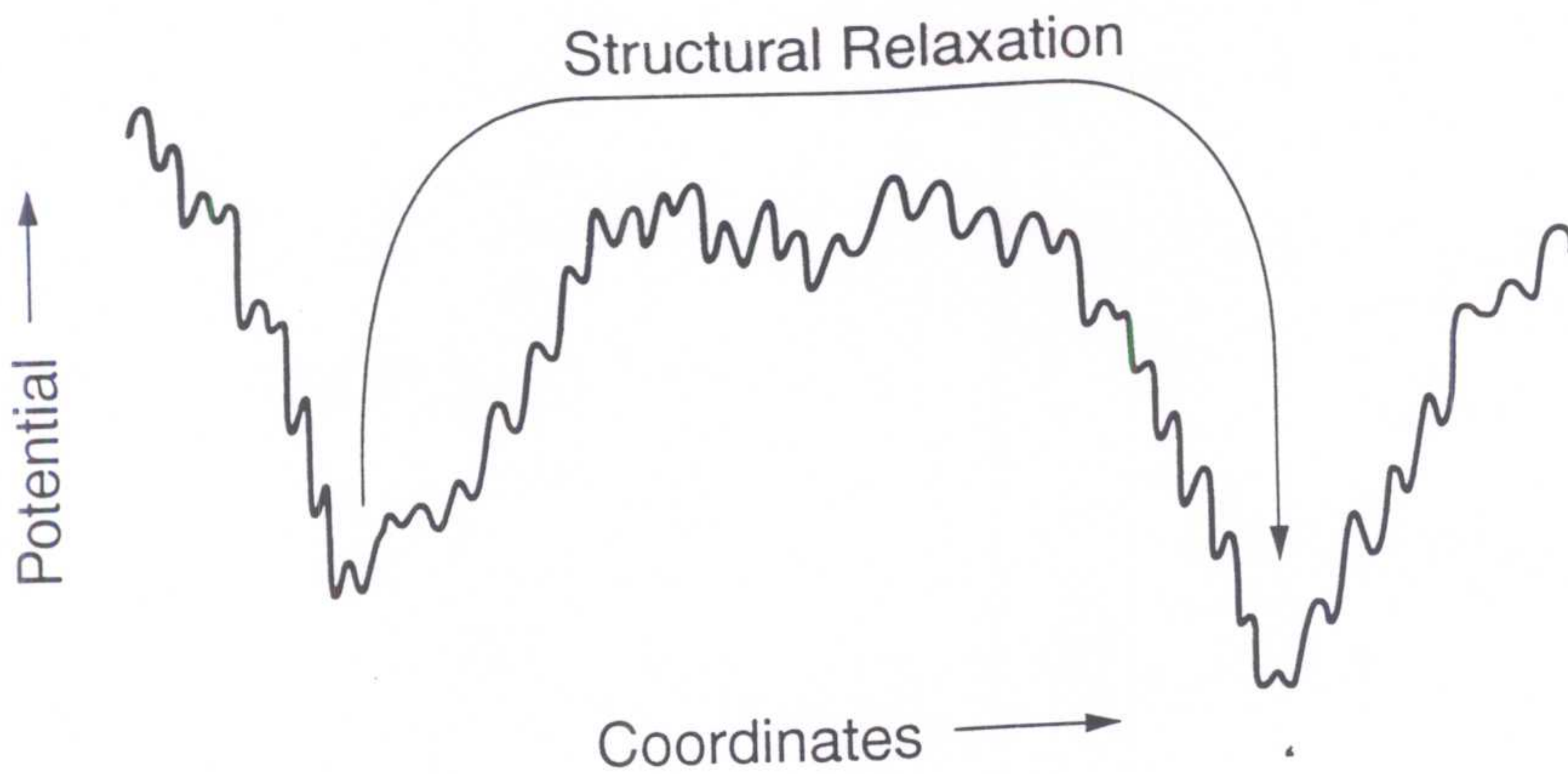
TEMPERATURE-DEPENDENT ABSORPTION MAXIMA (FRAGILE LIQUIDS):



STRUCTURAL RELAXATION



(a) Hot Liquid



(a) Strongly Supercooled Fragile Liquid

Research Problems

- How does bulk viscosity behave for glass-forming liquids? Does it track the temperature dependence of shear viscosity, and exhibit the same strong *versus* fragile distinctions?
- In what ways, and by how much, can glasses be rendered anisotropic by uniaxial stretching during solidification? What is the relation to nematic liquid crystals and the glasses that they form?
- Is there a simple, absolute, and non-arbitrary theoretical criterion for distinguishing true amorphous many-particle configurations from polycrystalline and defective-crystalline configurations?
- Upon classifying $T = 0$ amorphous configurations (inherent structures) by potential energy, is the lowest energy obtained unique or degenerate? What is the nature of structural excitations out of this set of lowest inherent structures?
- Develop a quantitative theory for thermal conduction of glasses.
- Is it possible to design a material whose shear viscosity remains constant or declines as the temperature is lowered (liquid sulfur example)?