Chapter 2. Thermophysical Properties of Polymers

Thermophysical properties include:

1. Volumetric properties
2. Calorimetric properties
3. Transition temperatures
4. Cohesive properties and solubility
5. Interfacial energy properties
6. Transport properties (diffusion et al.)

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Molar volumes of rubbery amorphous polymers

The rubbery amorphous state of polymers has the greatest correspondence with the liquid state of organic compounds. So it may be expected that the molar volume per structural unit of polymers in this state can be predicted by using the values of the group contributions mentioned in table 4.2.

$$V_r(298) = \sum_i V_i(298) .$$ (4.1a)

TABLE 4.2.
Group contributions to the molar volume of organic liquids at room temperature (cm^3/mol)

Groups	Investigators						
	Traube (1895)	Kurtz and Lipkin (1941)	Li et al. (1956)	Huggins (1954)	Davis and Gottlieb (1963)	Exner (1967)	Rheineck et al. (1968)
$-CH_2-$	16.1	16.3	16.5	16.5	16.6	16.6	16.5
$-CH(CH_3)-$	32.2	32.6		32.3	33.2		33.5
$-C(CH_3)_2-$	48.3	48.8		47.6	49.8	49.7	
$-CH=CH-$	24.3	26.4		26.5	25.0		
$-CH=C(CH_3)-$	40.4	42.6		40.3	40.6		
$-CH(CH=CH_2)-$	40.4	42.6	43.9		40.6	43.7	43.5
$-C_6H_{10}-$	77.2	78.9			78.5		
$-CH(C_6H_{11})-$	93.3	95.2	97.4		94.1	95.1	94.5
$-CH(C_5H_9)-$	77.2	82.0	82.6			80.3	
$-C_6H_4-$	58.6	60.3			61.8		
$-CH(C_6H_5)-$	74.7	76.6	78.8		77.4	75.8	74.5

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TABLE 4.6

Group contributions for V_g compared with those for V_r (cm^3/mol)

Groups		V_g	V_r
bivalent	$-CH_2-$	15.85	16.45
	$-CH(CH_3)-$	33.35	32.65
	$-C(CH_3)_2-$	52.4	50.35
	$-C_6H_4-$	65.5	61.4
	$-CH(C_6H_5)-$	82.15	74.5
	$-C_6H_3(CH_3)-$	83.4	—
	$-C_6H_2(CH_3)_2-$	104.1	—
	$-C_6H_{10}-$	87.8	—
	$-CH(C_6H_{11})-$	100.15	—
	$-CHF-$	20.35	19.85
	$-CHCl-$	29.35	28.25
	$-CH(CN)-$	28.95	—
	$-O-$	10.0	8.5
	$-CO-$	13.4	—
	$-COO-$ (general)	23.0	24.6
	$-COO-$ (acrylic)	18.25	21.0
	$-O-CO-O-$	31.4	—
	$-CH(OH)-$	19.15	—
	$-CONH-$	24.9	—
	$-S-$	17.8	15.0
tetravalent	$-\overset{\mid}{\underset{\mid}{C}}-$	4.6	4.75
	(benzene ring, para)	56.3	—
trivalent	$-\overset{\mid}{CH}-$	9.45	9.85
	(benzene ring)	59.5	—
monovalent	$-CH_3$	23.9	22.8
	$-C_6H_5$	72.7	64.65
	$-C_6H_{11}$	90.7	—
	$-F$	10.9	10.0
	$-Cl$	19.9	18.4
	$-CN$	19.5	—
	$-OH$	9.7	—

Conversion factor: 1 cm^3/mol = 10^{-6} m^3/mol.

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TABLE 4.3.

Molar volumes of rubbery amorphous polymers at 25°C

Polymer	ρ_r (g/cm^3)	V_r (cm^3/mol) experimental	V_r (cm^3/mol) calculated
polyethylene	0.855	32.8	32.9
polypropylene	0.85	49.5	49.1
polybutene	0.86	65.2	65.8
polypentene	0.85	82.5	82.0
polyhexene	0.86	97.9	98.5
polyisobutylene	0.84	66.8	66.8
poly(5-phenylpentene)	1.05	139.2	140.3
poly(vinylidene chloride)	1.66	58.4	58.0
poly(tetrafluoroethylene)	2.00	50.0	49.5
poly(isopropyl vinyl ether)	0.924	93.2	90.3
poly(butyl vinyl ether)	0.927	108.0	107.0
poly(sec.-butyl vinyl ether)	0.924	108.3	106.7
poly(isobutyl vinyl ether)	0.93	107.6	106.7
poly(pentyl vinyl ether)	0.918	124.4	123.4
poly(hexyl vinyl ether)	0.925	138.6	139.9
poly(octyl vinyl ether)	0.914	171.0	172.8
poly(2-ethylhexyl vinyl ether)	0.904	172.9	172.5
poly(decyl vinyl ether)	0.883	208.7	205.7
poly(dodecyl vinyl ether)	0.892	238.1	238.6
poly(vinyl propionate)	1.02	98.1	90.2
poly(vinyl methyl sulphide)	1.18	62.8	64.1
poly(vinyl butyl sulphide)	0.98	118.6	113.5
poly(methyl acrylate)	1.22	70.6	70.1
poly(ethyl acrylate)	1.12	89.4	86.6
poly(butyl methacrylate)	1.053	135.0	137.2
poly(hexyl methacrylate)	1.007	169.1	170.1
poly(2-ethylbutyl methacrylate)	1.040	163.8	169.8
poly(1-methylpentyl methacrylate)	1.013	168.1	169.8

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TABLE 4.5.

Molar volumes of glassy amorphous polymers at 25°C

Polymer	ρ_g (g/cm³)	V_g (cm³/mol)	
		experimental	calculated
poly(4-methylpentene)	0.84	100.2	98.4
polystyrene	1.05	99.0	98.0
poly(α-methylstyrene)	1.065	111.0	117.1
poly(o-methylstyrene)	1.027	115.1	114.7
poly(p-methylstyrene)	1.04	113.7	114.7
poly(p-tert.-butylstyrene)	0.95	168.7	167.1
poly(m-trifluoromethylstyrene)	1.32	130.5	128.1
poly(4-fluoro-2-trifluoromethylstyrene)	1.43	132.9	133.0
poly(3-phenylpropene)	1.046	113.0	113.9
poly(vinyl chloride)	1.385	45.1	45.2
poly(chlorotrifluoroethylene)	1.92	60.7	61.8
poly(3,3,3-trifluoropropylene)	1.58	60.8	62.6
poly(vinylcyclohexane)	0.95	116.0	116.0
poly(vinyl alcohol)	1.26	35.0	35.0
poly(vinyl methyl ketone)	1.12	62.6	62.6
poly(vinyl acetate)	1.19	72.4	72.2
poly(vinyl chloroacetate)	1.45	83.1	84.1
poly(tert.-butyl acrylate)	1.00	128.2	119.9
poly(methyl methacrylate)	1.17	85.6	86.5
poly(ethyl methacrylate)	1.119	102.0	102.4
poly(propyl methacrylate)	1.08	118.7	118.2
poly(isopropyl methacrylate)	1.033	124.1	119.9
poly(sec.-butyl methacrylate)	1.052	135.2	135.7
poly(tert.-butyl methacrylate)	1.022	139.1	138.9
poly(isopentyl methacrylate)	1.032	151.4	151.6
poly(1-methylbutyl methacrylate)	1.030	151.7	151.6

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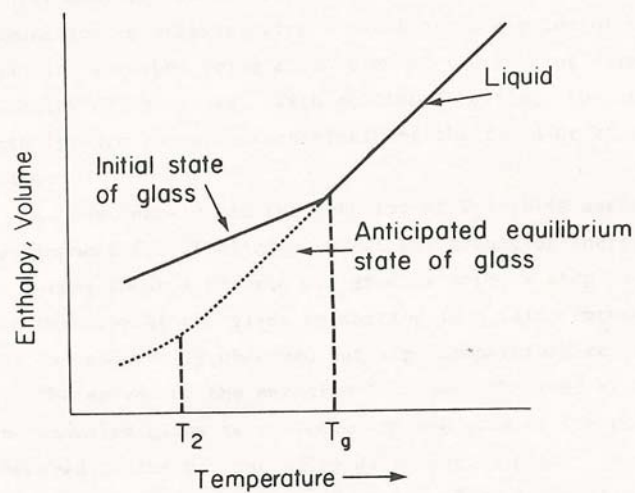- Physical aging of glassing polymers

FIG. 3. Schematic diagram of volume–enthalpy vs. temperature for a melt.

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I. Volumetric properties

1. Specific volume (=volume per unit weight)
2. Molar volume

This is the product of specific volume and molar weight.

$$V \equiv Mv \equiv \frac{M}{\rho} \quad \text{(dimension: cm}^3\text{/mol or m}^3\text{/mol)}$$

For polymers all molar functions are related to the structural unit. The following specified molar volumes are used:

2a) the molar volume at a certain standard temperature, e.g. room temperature: $V(298)$
2b) the *zero point molar volume*: $V^0(0) \ (\equiv V_c(0))$
This is the molar volume of the most stable condensed phase (crystal) at zero K.
2c) the *Van der Waals volume*: V_W
This is the volume enclosed by the electron clouds of the molecules.

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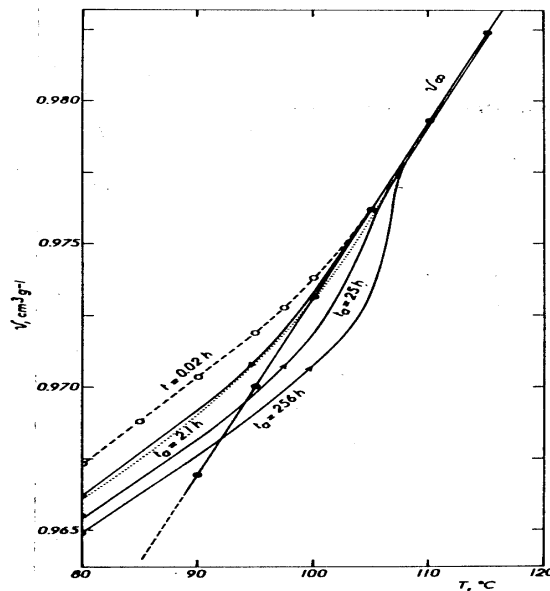
Fig. 3. Experimental $v(T)$ isobars for atactic polystyrene obtained on cooling ($q = -0.0025°C/sec$) and heating ($q = 0.017°C/sec$) after isothermal annealing at 80°C for various times t_a, as indicated. Discrete values of v, measured in equilibrium conditions (black points) and after quenching (open circles) from 105°C are also shown, together with the initial v_i values reached at 80°C (half circles) when heating is started. 8
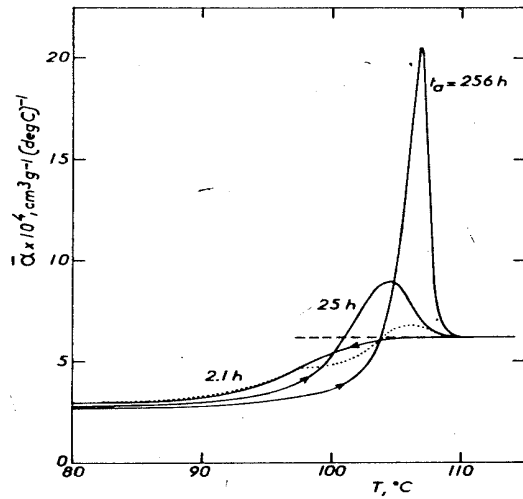
Fig. 4. Experimental $\bar{\alpha}$ vs. T isobars for polystyrene as derived from Figure 3. (Note that $\bar{\alpha}$ does not have the same lower limit ($\bar{\alpha}_g$) at 80°C).
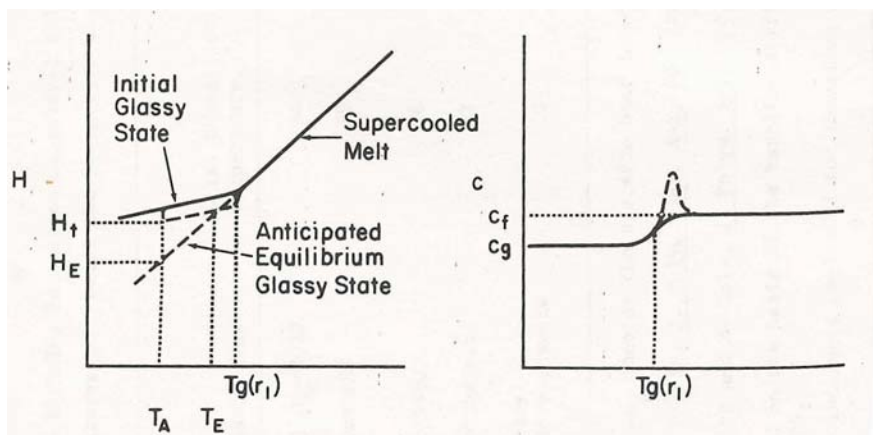
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- Enthalpy relaxation

FIG. 5. Enthalpy changes for annealed (– – –) and unannealed (——) glasses on heating at a heating rate r_1.

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Let $\delta = (v - v_\infty)/(v_i - v_\infty)$

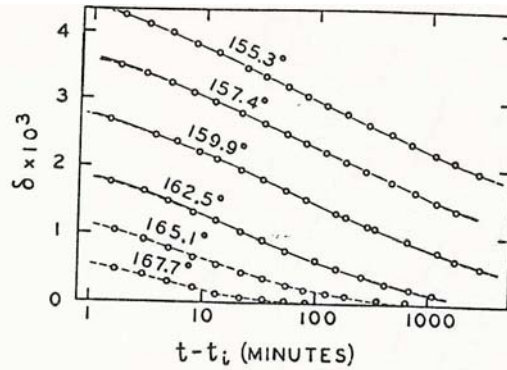$$d\delta/dt = -\delta/\tau$$

So, $\delta = \exp[-(t - t_i)/\tau]$

Fig. 4. Replotting of data from Fig. 1, taking into account the correction for the cooling period: (O) experimental data; (– –) calculated from eq. (7a); (——) calculated from eq. (7b).

Van der Waals volume

The Van der Waals volume of a molecule may be defined as the space occupied by this molecule, which is impenetrable to other molecules with normal thermal energies (i.e. corresponding with ordinary temperatures). For comparison with other quantities discussed in this chapter, the Van der Waals volume will be expressed in cm^3 per mole of unit structure.

$$\frac{V_r(298)}{V_W} = 1.60$$

$$\frac{V_g(298)}{V_W} = 1.55$$

$$\frac{V_c(298)}{V_W} = 1.435$$

$$\frac{V^0(0)}{V_W} = \frac{V_c(0)}{V_W} \approx 1.3.$$

TABLE 4.9

Van der Waals volume contributions (cm^3/mol)

Group	Bondi	Slonimskii et al.	Most probable value	$\frac{V_g}{V_W}$	$\frac{V_r}{V_W}$
$-CH_2-$	10.23	10.3	10.25	1.55	1.60
$-CH(CH_3)-$	20.45	20.8	20.5	1.63	1.59
$-C(CH_3)_2-$	30.67	31.3	31	1.69	1.62
$-CH=CH-$	16.94	18.1	17.5	–	1.59
$-CH=C(CH_3)-$	27.16	28.7	27.5	–	1.56
$-C_6H_{10}-$	53.34	54.5	54	1.63	–
$-CH(C_6H_{11})-$	63.58	64.8	64	1.56	–
$-C_6H_4-$	43.32	45.2	43.5	1.51	1.41
$-CH(C_6H_5)-$	52.62	55.7	53	1.55	1.41
$-CHF-$	13.0	13.4	13	1.57	1.53
$-CHCl-$	19.0	19.2	19	1.54	1.49
$-CF_2-$	15.3	16.6	16	1.65	1.55
$-CCl_2-$	27.8	28.2	28	1.59	1.48
$-CH(CN)-$	21.48	22.3	22	1.32	–
$-O-$	3.7	5.8	5.8	1.72	1.47
$-CO-$	11.7	11.2	11	1.22	–
$-COO-$	15.2	17.0	15	1.53	1.64
$-O-CO-O-$	18.9	23.0	19	1.65	–
$-CH(OH)-$	14.82	14.8	15	1.28	–
$-CONH-$	19.56	18.1	18	1.38	–
$-S-$	10.8	–	10	1.78	1.50

Conversion factor 1 $cm^3/mol = 10^{-6}$ m^3/mol

TABLE 4.10

Some empirical rules

Rule	Proposed by	Formula No.
$\alpha_l - \alpha_g \approx 5 \times 10^{-4}\ K^{-1}$	Tobolsky/Bueche (1960/1962)	(4.8)
$\alpha_l T_g \approx 0.16$	Boyer and Spencer (1944)	(4.9)
$\alpha_c T_m \approx 0.11$	Bondi (1968d)	(4.10)
$(\alpha_l - \alpha_g) T_g \approx 0.115$	Simha and Boyer (1962)	(4.11)

$$\alpha = \frac{1}{\upsilon}\left(\frac{\partial \upsilon}{\partial T}\right)_P$$

One of the most suitable expressions to represent the pVT behaviour of liquids, including polymeric liquids, is the Tait-relation:

$$\frac{V(p=1) - V(p)}{V(p=1)} = C \ln\left(1 + \frac{p}{B'}\right) \tag{4.17}$$

where p is the pressure in bar, C is a dimensionless constant ($C \approx 0.1$) and B' is a temperature dependent constant with the same basic dimension as pressure. Simha et al. (1973) have shown that C is indeed almost constant ($C = 0.0894$) and that the constant B' can be expressed by

$$B' = b_1 \exp(-b_2 T') \tag{4.18}$$

where b_1 and b_2 are empirical constants and T' is the temperature in °C. Substituting (4.18) into (4.17) gives:

$$\frac{V(p=1) - V(p)}{V(p=1)} = C \times 2.3 \log\left\{1 + \frac{p}{b_1} \exp(b_2 T')\right\} \tag{4.19}$$

TABLE 4.13

Constants of the Tait-equation for polymer melts

Polymer	$C \times 10^2$	b_1 (10^3 bar)	b_2 $(10^{-3} (°C)^{-1})$
polyethylene (ld)	9.70	1.99	5.10
polyisobutylene	8.71	1.91	4.15
polystyrene	(8.94)	2.44	4.14
poly(vinyl chloride)	(8.94)	3.52	5.65
poly(methyl methacrylate)	(8.94)	3.85	6.72
poly(vinyl acetate)	10.46	2.23	3.43
poly(dimethyl siloxane)	10.09	1.04	5.85

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II. Calorimetric properties

1. Heat capacity

The following notations can be formulated:

1. *Specific heat capacity at constant volume*

$$c_v = \left(\frac{\partial U}{\partial T}\right)_v \qquad \text{(dimension: J/kg · K)}$$

2. *Specific heat capacity at constant pressure*

$$c_p = \left(\frac{\partial (U+pV)}{\partial T}\right)_p = \left(\frac{\partial H}{\partial T}\right)_p \qquad \text{(dimension: J/kg · K)}$$

3. *Molar heat capacity at constant volume*

$$C_v = Mc_v \qquad \text{(dimension: J/mol · K)}$$

4. *Molar heat capacity at constant pressure*

$$C_p = Mc_p = \left(\frac{\partial H}{\partial T}\right)_p \qquad \text{(dimension: J/mol · K)}$$

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where **H** is the enthalpy (heat content) per mol.

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TABLE 5.1

Group contributions to the molar heat at 25°C (J/mol · K)

Group	C_p^s (Satoh)	C_p^l (Shaw)	C_p^s/R per atom	C_p^l/R per atom
$-CH_3$	30.9	36.9	0.92	1.10
$-CH_2-$	25.35	30.4	1.01	1.21
$-CH-$	15.6	20.95	0.93	1.25
$-C-$	6.2	7.4	0.74	0.88
$=CH_2$	22.6	21.8	0.90	0.87
$=CH-$	18.65	21.4	1.11	1.28
$=C-$	10.5	15.9	1.25	1.90
$-CH_2-$ (5 ring)	19.9	26.4	0.79	1.05
$-CH_2-$ (6 ring)	18.0	26.4	0.71	1.03
CH_{ar}	15.4	22.2	0.92	1.33
$C_{ar}-$	8.55	12.2	1.02	1.45
(ring)	85.6	123.2	0.94	1.35
(ring)	78.8	113.1	0.95	1.36
(ring)	65.0	93.0	0.98	1.40
$-F$	(21.4)	(21.0)	2.55	2.50
$-Cl$	27.1	(39.8)	3.23	4.75
$-Br$	26.3	–	3.14	–
$-I$	22.4	–	2.67	–
$-CN$	(25)	–	1.50	–
$-OH$	17.0	44.8	1.01	2.68
$-O-$	16.8	35.6	2.01	<4.25
$-CO-$	23.05	52.8	1.38	3.15
$-COOH$	(50)	98.9	1.50	2.95
$-COO-$	(46)	65.0	1.83	2.58
$-NH_2$	20.95	–	0.83	–
$-NH-$	14.25	(31.8)	0.85	1.90
$>N-$	17.1	(44.0)	2.04	5.25
$-NO_2$	41.9	–	1.67	–
$-CONH-$	(38–54)	(90.1)	1.12–1.63	2.68
$-S-$	24.05	44.8	2.37	5.35
$-SH$	46.8	52.4	2.78	3.12
$-SO_2-$	(50)	–	2.00	–

TABLE 5.2

Experimental and calculated heat capacities of polymers

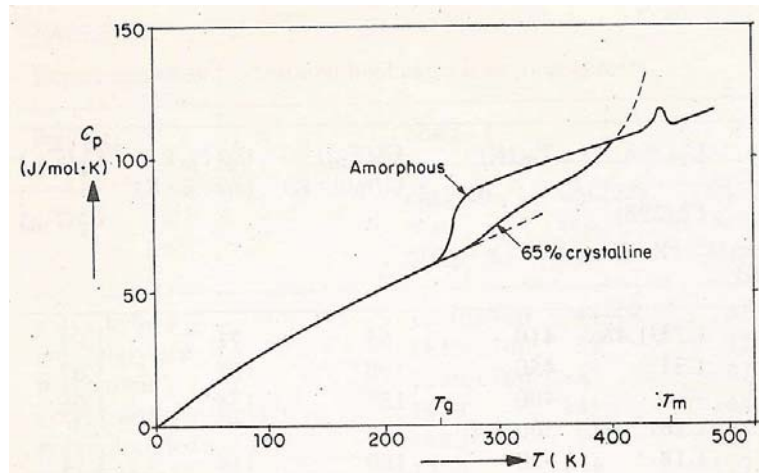| Polymer	Solid				
	$c_p^s(298)$ exp. (J/kg · K)	$C_p^s(298)$ exp. (J/mol · K)	$C_p^s(298)$ Satoh (J/mol · K)	$C_p^s(200)$ exp. (J/mol · K)	$C_p^s(200)$ Satoh (J/mol · K)
polyethylene	1550/1760	44/49	51	34	33
polypropylene	1630/1760	69	72	48	46
polybutene	1550/1760	>87	97	69	62
poly(4-methylpentene)	1680	141	144	100	91
polyisobutylene	1680	94	93	65	58
polystyrene	1220	128	127	84	81
poly(vinyl chloride)	960/1090	60/68	68	42/49	47
poly(vinylidene chloride)	–	–	86	70	60
poly(tetrafluoroethylene)	~960	96	(98)	69	–
poly(chlorotrifluoroethylene)	920	105	(104)	–	–
poly(vinyl alcohol)	1300	57	58	39	37
poly(vinyl acetate)	~1470	~127	(118)	88	–
poly(methyl acrylate)	1340	115	(118)	–	–
poly(ethyl acrylate)	1450	145	(143)	–	–
poly(butyl acrylate)	1640	210	(194)	–	–
poly(methyl methacrylate)	1380	138	(139)	~101	–
poly(ethyl methacrylate)	1450	166	(165)	–	–
poly(butyl methacrylate)	1680	239	(215)	–	–

Fig. 5.1. Molar heat capacity of polypropylene.

The slopes of the heat capacity lines for solid polymers show a mean value

$$\frac{1}{C_p^s(298)} \cdot \frac{dC_p^s}{dT} = 3 \times 10^{-3}$$

with a mean deviation of 5%.

For liquid polymers, an analogous expression may be used, but much larger deviations occur. In this case

$$\frac{1}{C_p^l(298)} \cdot \frac{dC_p^l}{dT} = 1.2 \times 10^{-3}$$

with a mean deviation of 30%. Nevertheless, if experimental data are lacking, the temperature function of the heat capacity may be approximated with these mean values, so that:

$$C_p^s(T) = C_p^s(298)[1 + 3 \times 10^{-3}(T - 298)] = C_p^s(298)[0.106 + 3 \times 10^{-3}T] \qquad (5.1)$$

$$C_p^l(T) = C_p^l(298)[1 + 1.2 \times 10^{-3}(T - 298)] = C_p^l(298)[0.64 + 1.2 \times 10^{-3}T] \qquad (5.2)$$

TABLE 5.3
Temperature function of the molar heat capacity (K^{-1})

Polymer	$\dfrac{1}{C_p^s(298)}\dfrac{dC_p^s}{dT}$	$\dfrac{1}{C_p^l(298)}\dfrac{dC_p^l}{dT}$
polyethylene	3.0×10^{-3}	1.0×10^{-3}
polybutene	3.1×10^{-3}	1.4×10^{-3}
poly(4-methylpentene)	3.0×10^{-3}	—
polyisobutylene	3.3×10^{-3}	2.2×10^{-3}
polystyrene	3.4×10^{-3}	1.2×10^{-3}
poly(vinyl chloride)	2.8×10^{-3}	—
poly(vinyl acetate)	2.9×10^{-3}	—
poly(methyl acrylate)	2.6×10^{-3}	1.1×10^{-3}
poly(ethyl acrylate)	2.7×10^{-3}	1.5×10^{-3}
poly(butyl acrylate)	3.0×10^{-3}	1.5×10^{-3}
poly(methyl methacrylate)	3.0×10^{-3}	1.5×10^{-3}
poly(ethyl methacrylate)	3.0×10^{-3}	—
poly(butyl methacrylate)	3.2×10^{-3}	1.9×10^{-3}
polybutadiene	3.1×10^{-3}	—
polyisoprene	3.0×10^{-3}	1.8×10^{-3}
poly(ethylene oxide)	2.6×10^{-3}	0.5×10^{-3}
poly(tetramethylene oxide)	2.9×10^{-3}	1.0×10^{-3}
poly(propylene oxide)	2.9×10^{-3}	1.4×10^{-3}
poly(phenylene oxide)	2.7×10^{-3}	0.9×10^{-3}
poly(ethylene sebacate)	—	1.2×10^{-3}
poly(hexamethylene adipamide)	3.0×10^{-3}	0.5×10^{-3}
poly(bisphenol-A carbonate)	3.2×10^{-3}	1.4×10^{-3}

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$$c_v = c_p - Tv\frac{\alpha^2}{\kappa}$$

where v = specific volume, α = expansion coefficient, κ = compressibility.

B. LATENT HEAT OF CRYSTALLIZATION AND FUSION

The latent heat of fusion (crystallization) or the enthalpy difference

$$H_l(T_m) - H_c(T_m) = \Delta H_m(T_m)$$

$$\Delta S_m = \frac{\Delta H_m}{T_m}, \quad \Delta S_m = \sum n_i \Delta s_i$$

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TABLE 5.4

Enthalpy and entropy of fusion for some polymers

Polymer	ΔH_m (J/mol) literature	ΔH_m (J/mol) predicted (table 5.5)	T_m (K)	ΔS_m (J/mol · K)
polyethylene	7500–8400	7600	414	18.0–20.1
polypropylene	8800–10900	10100	456	19.3–23.9
polystyrene	8400–10100	–	513	16.3–19.7
poly(vinyl chloride)	11300	–	558	20.1
poly(vinyl fluoride)	7500	–	473	15.9
poly(tetrafluoroethylene)	5900	–	600	9.6
poly(chlorotrifluoroethylene)	5000–8800	–	491	10.1–17.9
poly(vinyl alcohol)	6900	–	531	13.0
polyacrylonitrile	5000	–	590	8.4
polybutadiene	9200–10100	9700	421	21.8–23.9
polyisoprene	12600	12200	309–347	36.0–40.6
polychloroprene	8400	–	316	26.4
polyformaldehyde	7100	5500	460	15.5
poly(ethylene oxide)	8400–9200	9300	340	24.7–27.2
poly(tetramethylene oxide)	12600	16900	310	40.6
poly(propylene oxide)	8400	11800	348	23.9
polyester 2, 6	15900	14400	320	49.9

TABLE 5.5

Approximate values of group contribution to the heat of fusion of polymers

Group	Group contribution (J/mol)	Group	ΔS_i (J/mol · K)
$-CH_2-$	3800	$-CH_2-$	8.4
$-CH(CH_3)-$	6300		
$-CH=CH-$	2100		
$-CH=C(CH_3)-$	4600		
⟨benzene ring⟩	22200	⟨benzene ring⟩	29.3
$-O-$	1700	$-O-$	7.5
$-COO-$	–4200	$-COO-$	0.0
$-CONH-$	2900	$-CONH-$	0.0

Conversion factor: 1 J/mol = 0.24 cal/mol

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In determining the course of enthalpy and entropy of a substance with temperature it is usual to start from very accurate specific heat measurements. Enthalpy and entropy may then be calculated by integration:

$$H(T) = H(0) + \int_0^T C_p\,dT + \sum \Delta H_i \qquad (5.7)$$

$$S(T) = S(0) + \int_0^T \frac{C_p}{T}\,dT + \sum \Delta S_i \qquad (5.8)$$

where $H(0)$ and $S(0)$ are the enthalpy and entropy at 0 K and ΔH_i and ΔS_i are the enthalpy and entropy changes at first order phase transitions.
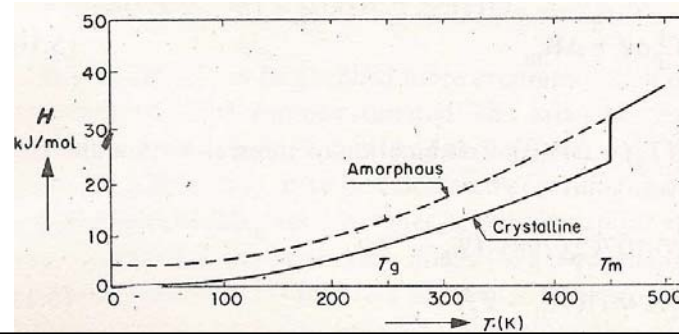
$$H_c(T) = H_c(0) + \int_0^T C_p^s\,dT \qquad (T < T_m)$$

$$H_l(T) = H_c(0) + \int_0^{T_m} C_p^s\,dT + \int_{T_m}^T C_p^l\,dT + \Delta H_m$$

III. Transition Temperature

$$T_g = T_g(\infty) - \frac{A}{\overline{M}_n}$$

where $T_g(\infty)$ is the value of T_g for very high molecular weights.

A theoretical derivation based on the Gibbs–Di Marzio (1958) theory of the glass transition leads to the conclusion that for the series of polyalkyl methacrylates

$$T_g(\text{syndiotactic}) - T_g(\text{isotactic}) = \text{constant} \approx 112°$$

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T_g of stereoregular polyalkyl methacrylates (K)		
Polymer	T_g syndio	T_g iso
poly(methyl methacrylate)	433	316
poly(ethyl methacrylate)	393	281
poly(isopropyl methacrylate)	412	300
poly(butyl methacrylate)	361	249
poly(isobutyl methacrylate)	393	281
poly(cyclohexyl methacrylate)	436	324

$$\frac{dT_g}{dp} = \frac{T_g V(T_g)\Delta\alpha}{\Delta C_p} = \frac{\Delta\kappa}{\Delta\alpha}$$

or

$$\Delta C_p \Delta\kappa = T_g V(T_g)(\Delta\alpha)^2$$

where

T_g = glass transition temperature
p = pressure
$V(T_g)$ = molar volume at T_g
$\Delta\alpha$ = $\alpha_1 - \alpha_g$ = difference in thermal expansion coefficient at T_g
ΔC_p = $C_p^l(T_g) - C_p^s(T_g)$ = difference in molar heat capacity at T_g
$\Delta\kappa$ = $\kappa_1 - \kappa_g$ = difference in compressibility at T_g.

$$T_g = \frac{Y_g}{M} = \frac{\sum_i Y_{gi} + Y_g(I_{xi})}{M}$$

where I_x is

defined as the number of main chain atoms in the polar group (X) divided by the number of chain atoms of this group plus those of the directly connected methylene chains. For the configuration

$$-(CH_2)_{n_1} -X-(CH_2)_{n_2}-$$
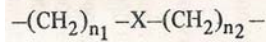
in which the characteristic group X contains n_x chain atoms, the formula of I_x is:

$$I_x = \frac{n_x}{n_x + n_1 + n_2}$$
(6.6)

Example 6.1

Estimate the glass transition temperature of poly(ethylene terephthalate). Structural formula:

$$I = \frac{2}{2+2} = 0.5$$
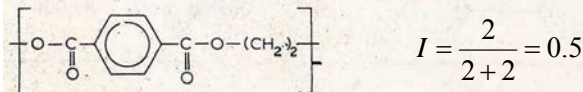
Group contributions to Y_g (K · g/mol)

Group	Y_{gi}	Group	Y_{gi}	Group	Y_{gi}	$Y_g(I_x)$
$-CH_2-$	2,700	(phenyl)	32,000	$-O-$	4,000	—
$-CH(CH_3)-$	8,000	(Cl-phenyl)	51,000	$-\overset{O}{\underset{\parallel}{C}}-$	27,000	—
$-CH(C_2H_5)-$	10,500	(CH_3-phenyl)	35,000	$-\overset{O}{\underset{\parallel}{C}}-O-$	8,000	12,000 I
$-CH(C_3H_7)-$	13,100	(di-CH_3-phenyl)	(55,000)	$-O-\overset{O}{\underset{\parallel}{C}}-O-$	16,000	10,000 I
$-CH(C_6H_5)-$	35,000	(CH_3-phenyl)	28,000	$-\overset{O}{\underset{\parallel}{C}}-O-\overset{O}{\underset{\parallel}{C}}-$	(20,000)	?
$-CH(C_6H_4CH_3)-$	42,000	(di-CH_3-phenyl)	30,000	$-S-$	7,500	—
$-CH(OCH_3)-$	11,900			$-\overset{O}{\underset{O}{\overset{\parallel}{S}}}-$	(58,000)	?
$-CH(COOCH_3)-$	21,300	(naphthyl)	7,000	$-\overset{O}{\underset{O}{\overset{\parallel}{S}}}-O-$	(31,000)	?
$-C(CH_3)_2-$	8,400[1] / 15,000	(naphthyl)	58,000	$-\overset{O}{\underset{\parallel}{C}}-NH-$	12,000	$1,800\, I^{-1} + 2 \times 10^6 \frac{n_\phi}{M}$
$-C(CH_3)(C_2H_5)-$	17,700			$-O-\overset{O}{\underset{\parallel}{C}}-NH-$	(25,000)	?
$-C(CH_3)(C_6H_5)-$	(50,000)	(cyclohexyl trans)	31,000	$-NH-\overset{O}{\underset{\parallel}{C}}-NH-$	20,000	$2,100\, I^{-1}$
$-C(CH_3)(COOCH_3)-$	35,100			CH_3		
$-CH(OH)-$	13,000			$-Si-$	8,000	—
$-CHF-$	11,000			CH_3		
$-CHCl-$	20,000					
$-CF_2-$	13,000					
$-CCl_2-$	25,000					
$-CFCl-$	23,000					

[1] In polyisobutylene only!

TABLE 6.4
Experimental and calculated values of T_g for a number of polymers (K)

Polymer	T_g exp.	T_g calc.
poly(methylene oxide)	188/243	223
poly(ethylene oxide)	206/246	214
poly(trimethylene oxide)	195/228	209
poly(tetramethylene oxide)	185/194	206
poly(paraxylylene disulphide)	296	312
poly(decamethylene tetrasulphide)	197	212
poly(ethylene adipate)	203/233	222
poly(ethylene dodecate)	202	202
poly(decamethylene adipate)	217	200
poly(ethylene terephthalate)	342/350	341
poly(decamethylene terephthalate)	268/298	260
poly(diethyleneglycol malonate)	244	248
poly(diethyleneglycol octadecanedioate)	205	198
poly(metaphenylene isophthalate)	411/428	400
poly(4,4'-methylene diphenylene carbonate)	393/420	410
poly(4,4'-isopropylidene diphenylene carbonate)	414/423	413
poly(4,4'-tetramethylene dibenzoic anhydride)	319	339
poly(4,4'-methylenedioxy dibenzoic anhydride)	357	351
poly(hexamethylene adipamide)	318/330	321
poly(decamethylene sebacamide)	319/333	320
poly(heptamethylene terephthalamide)	383/396	410
poly(paraphenylene diethylene sebacamide)	378	370

$$T_m = \frac{Y_m}{M} = \frac{\sum_i Y_{mi} + \sum Y_m(I_x) + \sum Y_m(ODD)}{M}$$

Group contributions to Y_m (K · g/mol)

| Group	Y_{mi}	Group	Y_{mf}	Group	Y_{mi}	$Y_m(I_x)$	$Y_m(ODD)$
–CH₂–	5,700	(para-phenylene)	50,000	–O–	–3,300	$33,000\,I$ [1]	–300
–CH(CH₃)– {symm. / asymm.}	13,000 / –7,000	(tolylene, CH₃)	35,000	–C(=O)–	?		
–CH(C₆H₅)–	48,000	(CH₃, ø)	153,000	–C(=O)–O–	5,000	$30,000\,I$	–1,500
–CH(OCH₃)–	19,000			–O–C(=O)–O–	7,000	$30,000\,I$	(–1,500)
–CH(COOCH₃)–	—	(naphthylene)	25,000	–C(=O)–O–C(=O)–	14,000	$36,000\,I$	–1,500
–C(CH₃)₂–	12,000			–S–	1,700	$60,000\,I$ [1]	–1,000
–C(CH₃)(COOCH₃)–	(37,500)		13,000	–S–S–	5,000	$60,000\,I$ [1]	–1,000
–CH(OH)–	18,000			–S(=O)(=O)–	?		
–CHF–	14,700	{trans / cis}	50,000 / 26,000	–C(=O)–NH–	48,000	$-6,000\,I^{-1/2}$	–2,500
–CHCl–	23,700			–O–C(=O)–NH–	42,000	$-6,000\,I^{-1/2}$	–2,500
–CF₂–	23,700			–NH–C(=O)–NH–	55,000	$-6,000\,I^{-1/2}$	–2,500
–CCl₂–	41,700						
–CFCl–	32,700						

[1] Not valid at $I_x = 1$.

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TABLE 6.10

Experimental and calculated values of T_m for a number of polymers (K)

Polymer	T_m exp.	T_m calc.
poly(methylene oxide)	333/473	426
poly(ethylene oxide)	335/349	334
poly(trimethylene oxide)	308	309
poly(tetramethylene oxide)	308/333	322
poly(tetramethylene acetal)	296	317
poly(decamethylene acetal)	330	328
poly(ethylene sulphide)	418/483	418
poly(decamethylene sulphide)	351/365	358
poly(ethylene disulphide)	386/418	396
poly(decamethylene disulphide)	318/332	331
poly(ethylene adipate)	320/338	344
poly(decamethylene adipate)	343/355	344
poly(decamethylene sebacate)	344/358	349
poly(ethylene terephthalate)	538/557	528
poly(decamethylene terephthalate)	396/411	418
poly(paraphenylene dimethylene adipate)	343/354	357
poly(tetramethylene anhydride)	350/371	364
poly(hexadecamethylene anhydride)	368	366
poly(tetramethylene carbonate)	332	320
poly(decamethylene carbonate)	328/378	345

$$\frac{T_g}{T_m} = \begin{cases} \frac{1}{2} & \text{for symmetrical polymers} \\ \frac{2}{3} & \text{for unsymmetrical polymers} \end{cases}$$
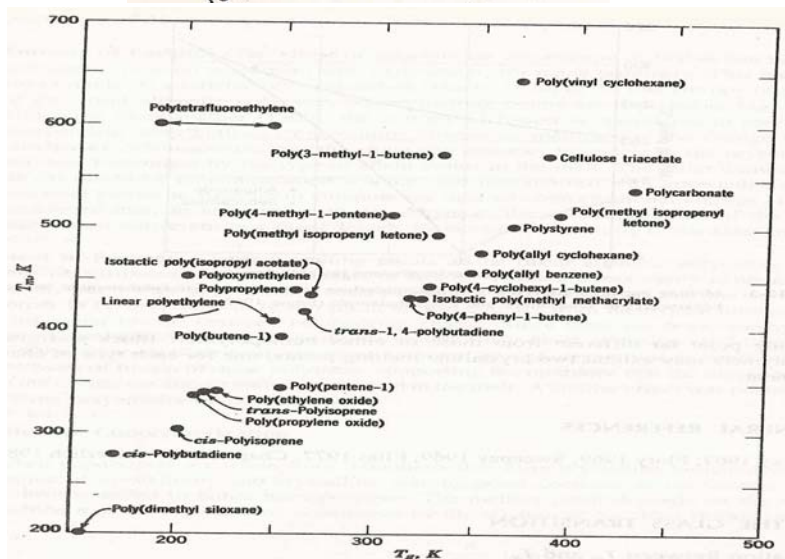
FIG. 12-4. Relation between T_m and T_g for various polymers (Boyer 1963).

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IV. Cohesive properties and solubility

The cohesive energy E_{coh} of a substance in a condensed state is defined as the increase in internal energy U per mole of substance if all the intermolecular forces are eliminated:

the cohesive energy $\equiv E_{coh} = \Delta U$ (dimension: J/mol)

Directly related to the cohesive energy are the quantities

cohesive energy density: $e_{coh} \equiv \dfrac{E_{coh}}{V}$ (at 298 K)   (dimension: J/cm^3)

solubility parameter $\delta = \left(\dfrac{E_{coh}}{V}\right)^{1/2} \equiv e_{coh}^{1/2}$ (at 298 K)   (dimension: J$^{1/2}$/cm$^{3/2}$)

Determination of E_{coh}

For liquids of low molecular weight, the cohesive energy is closely related to the molar heat of evaporation ΔH_{vap} (at a given temperature):

$$E_{coh} = \Delta U_{vap} = \Delta H_{vap} - p\Delta V \approx \Delta H_{vap} - RT \tag{7.1}$$

Cohesive energy density of polymers can be determined by swelling or dissociation experiments.

Fig. 7.1. Equilibrium swelling as a function of the solubility parameter of the solvent for linear and cross-linked polystyrene.

TABLE 7.4

Group contributions to E_{coh} and V according to Fedors

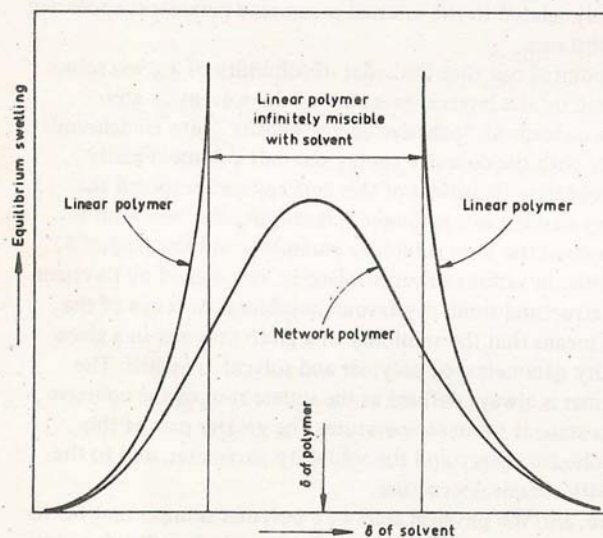| Group	E_{coh} (J/mol)	V (cm³/mol)
—CH₃	4710	33.5
—CH₂—	4940	16.1
⟩CH—	3430	−1.0
⟩C⟨	1470	−19.2
H₂C=	4310	28.5
—CH=	4310	13.5
⟩C=	4310	−5.5
HC≡	3850	27.4
—C≡	7070	6.5
Phenyl	31940	71.4
Phenylene (o, m, p)	31940	52.4
Phenyl (trisubstituted)	31940	33.4
Phenyl (tetrasubstituted)	31940	14.4
Phenyl (pentasubstituted)	31940	−4.6
Phenyl (hexasubstituted)	31940	−23.6
Ring closure 5 or more atoms	1050	16
Ring closure 3 or 4 atoms	3140	18
Conjugation in ring for each double bond	1670	−2.2
Halogen attached to carbon atom with double bond	−20% of E_{coh} of halogen	4.0
—F	4190	18.0
—F (disubstituted)	3560	20.0
—F (trisubstituted)	2300	22.0
—CF₂— (for perfluoro compounds)	4270	23.0
—CF₃ (for perfluoro compounds)	4270	57.5
—Cl	11550	24.0

TABLE 7.3

Cohesive energy of polymers

Polymer	δ ($J^{1/2}/cm^{3/2}$) from	δ to	V (cm³/mol)	E_{coh} (from δ) (J/mol) from	to	E_{coh} (calculated) (J/mol) Dunkel	Di Benedetto	Hayes	Fedors
Polyethylene	15.8	17.1	32.9	8200	9600				
Polypropylene	16.8	18.8	49.1	13900	17400	8300	7200	8300	9880
Polyisobutylene	16.0	16.6	66.8	17100	18400	10020	–	11270	13080
Polystyrene	17.4	19.0	98.0	29700	35400	11730	13990	16050	15850
Poly(vinyl chloride)	19.2	22.1	45.2	16700	22100	33480	41060	34270	40310
Poly(vinyl bromide)	19.4	–	48.6	18300	–	16810	16930	21660	19920
Poly(vinylidene chloride)	20.3	25.0	58.0	23900	36300	–	–	–	23860
Poly(tetrafluoroethylene)	12.7	–	49.5	8000	–	25310	–	15460	25670
Poly(chlorotrifluoroethylene)	14.7	16.2	61.8	13400	16200	19840	–	9640	17180
Poly(vinyl alcohol)	25.8	29.1	35.0	23300	29600	25460	–	–	23250
Poly(vinyl acetate)	19.1	22.6	72.2	26300	36900	32940	–	–	38170
Poly(vinyl propionate)	18.0	–	90.2	29200	–	26030	28990	25430	31080
Poly(methyl acrylate)	19.9	21.3	70.1	27800	31800	30180	32590	29580	36020
Poly(ethyl acrylate)	18.8	19.2	86.6	30600	31900	26030	28990	25430	31080
Poly(propyl acrylate)	18.5	–	103.1	35300	–	30180	32590	29580	36020
Poly(butyl acrylate)	18.0	18.6	119.5	38700	41300	34330	36190	33730	40960
Poly(isobutyl acrylate)	17.8	22.5	119.3	37800	60400	38480	39790	37880	45900
Poly(2,2,3,3,4,4,4-heptafluorobutyl acrylate)	13.7	–	148.0	27800	–	36050	–	36700	44160
Poly(methyl methacrylate)	18.6	26.2	86.5	29900	59400	61110	–	–	56860
Poly(ethyl methacrylate)	18.2	18.7	102.4	33900	35800	27740	–	30210	33830
Poly(butyl methacrylate)	17.8	18.4	137.2	43500	46500	31890	–	34360	38770
Poly(isobutyl methacrylate)	16.8	21.5	135.7	38300	62700	40190	–	42660	48650
Poly(tert.-butyl methacrylate)	17.0	–	138.9	40100	–	37760	–	41480	46910
Poly(benzyl methacrylate)	20.1	20.5	151.2	61100	63500	35320	–	42110	44720
Poly(ethoxyethyl methacrylate)	18.4	20.3	145.6	49300	60000	55350	–	–	66000
Polyacrylonitrile	25.6	31.5	44.8	29400	44500	47020	–	49490	52000
Polymethacrylonitrile	21.9	–	63.9	30600		–	–	28280	33900

• The solubility parameter

$$\Delta G_M = \Delta H_M - T\Delta S_M \tag{7.2}$$

where
ΔH_M = enthalpy of mixing
ΔS_M = entropy of mixing.
As ΔS_M is generally positive, there is a certain limiting positive value of ΔH_M below which dissolution is possible.

As early as 1916 Hildebrand tried to correlate solubility with the cohesive properties of the solvents. In 1949 he proposed the term solubility parameter and the symbol δ, as defined in the beginning of this chapter.

According to Hildebrand, the enthalpy of mixing can be calculated by

$$\Delta h_M = \phi_1\phi_2(\delta_1 - \delta_2)^2 \tag{7.3}$$

where
Δh_M = enthalpy of mixing per unit volume
ϕ_1 and ϕ_2 = volume fractions of components 1 and 2
δ_1 and δ_2 = solubility parameters of components 1 and 2.

Formally, the cohesive energy may be divided into three parts, corresponding with the three types of interaction forces

$$E_{coh} = E_d + E_p + E_h \tag{7.4}$$

where
E_d = contribution of dispersion forces
E_p = contribution of polar forces
E_h = contribution of hydrogen bonding
The corresponding equation for the solubility parameter is

$$\delta^2 = \delta_d^2 + \delta_p^2 + \delta_h^2 \tag{7.5}$$

The equivalent of eq. (7.3) becomes

$$\Delta h_M = \phi_1\phi_2[(\delta_{d1} - \delta_{d2})^2 + (\delta_{p1} - \delta_{p2})^2 + (\delta_{h1} - \delta_{h2})^2] \tag{7.6}$$

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TABLE 7.7

Hansen's specified solubility parameters for some polymers

Polymer	δ	δ_d	δ_p	δ_h
Polyisobutylene	17.6	16.0	2.0	7.2
Polystyrene	20.1	17.6	6.1	4.1
Poly(vinyl chloride)	22.5	19.2	9.2	7.2
Poly(vinyl acetate)	23.1	19.0	10.2	8.2
Poly(methyl methacrylate)	23.1	18.8	10.2	8.6
Poly(ethyl methacrylate)	22.1	18.8	10.8	4.3
Polybutadiene	18.8	18.0	5.1	2.5
Polyisoprene	18.0	17.4	3.1	3.1

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V. Interfacial energy properties

Surface energy is a direct manifestation of intermolecular forces. The molecules at the surface of a liquid or a solid are influenced by unbalanced molecular forces and therefore possess additional energy, in contrast with the molecules inside the liquid or solid.

In liquids the surface energy manifests itself as an internal force which tends to reduce the surface area to a minimum. It is measured in units of force per unit length, or in units of energy per unit area.

The surface of a solid, like that of a liquid, possesses additional free energy, but owing to the lack of mobility at the surface of solids this free energy is not directly observable, it must be measured by indirect methods.

The additional free energy at the interface between two condensed phases is known as *interfacial energy*.

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Definitions

The specific *free surface energy* of a material is the excess energy per unit area due to the existence of the free surface; it is also the thermodynamic work to be done per unit area of surface extension.

In liquids the specific free surface energy is also called *surface tension*, since it is equivalent to a line tension acting in all directions parallel to the surface.

The *specific interfacial energy* or *interfacial tension* is the excess energy per unit area due to the formation of an interface (solid/liquid; solid/vapour).

The surface or interfacial tension is expressed in $J/m^2 (\equiv N/m)$ or more often in $mJ/m^2 (\equiv mN/m)$. The latter expression is identical with $erg/cm^2 (\equiv dyn/cm)$ in the c.g.s. unit system.

1. $$\kappa \gamma^{3/2} = 1.33 \times 10^{-8} \text{ (cgs units)}$$

    where κ is the compressibility

2. $$\delta = 4.1(\gamma/V^{1/3})^{0.43} \text{(cgs units)}$$

Calculation of surface tension from an additive function; the Parachor

The molar parachor is a useful means of estimating surface tensions. It is the following additive quantity:

$$P_S = \gamma^{1/4}\frac{M}{\rho} = \gamma^{1/4}V. \tag{8.4}$$

$$\gamma = \left(\frac{P_S}{V}\right)^4$$

TABLE 8.1
Atomic and structural contributions to the parachor

Unit	Values assigned by		
	Sugden	Mumford and Phillips	Quayle
CH$_2$	39.0	40.0	40.0
C	4.8	9.2	9.0
H	17.1	15.4	15.5
O	20.0	20.0	19.8
O$_2$ (in esters)	60.0	60.0	54.8
N	12.5	17.5	17.5
S	48.2	50.0	49.1
F	25.7	25.5	26.1
Cl	54.3	55.0	55.2
Br	68.0	69.0	68.0
I	91.0	90.0	90.3
Double bond	23.2	19.0	16.3–19.1
Triple bond	46.4	38.0	40.6
Three-membered ring	16.7	12.5	12.5
Four-membered ring	11.6	6.0	6.0
Five-membered ring	8.5	3.0	3.0
Six-membered ring	6.1	0.8	0.8
Seven-membered ring		−4.0	4.0

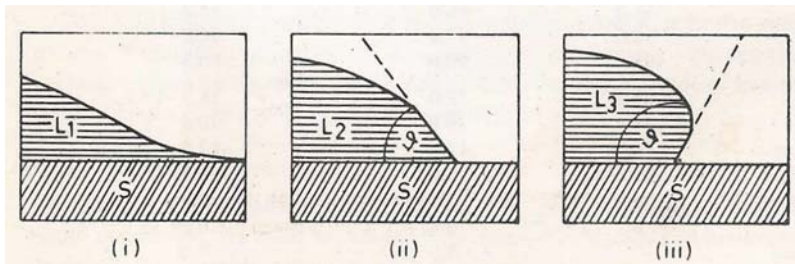• Interfacial tension between a solid and a liquid

Fig. 8.1. Contact angle of different liquids on a solid.

Young's equation $\quad \gamma_{lv} \cos\theta + \gamma_{sl} = \gamma_{sv}$

$$\gamma_1 \cos\vartheta = (\gamma_s - \gamma_{sl}) - (\gamma_s - \gamma_{sv}) = (\gamma_s - \gamma_{sl}) - \pi_{eq} \approx \gamma_s - \gamma_{sl} \qquad (8$$

The assumption $\pi_{eq} \approx 0$ is allowed for normal polymeric surfaces. $\gamma_1 \cos\vartheta$ is called the adhesion tension. Complete wetting occurs when $\cos\vartheta = 1$ or $\vartheta = 0°$.

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important relationship between γ_s, γ_l and γ_{sl}:

$$\gamma_{sl} = \gamma_s + \gamma_l - 2\Phi(\gamma_s\gamma_l)^{1/2}$$

where

$$\Phi \approx \frac{4(V_sV_l)^{1/3}}{(V_s^{1/3} + V_l^{1/3})^2}.$$

Combining eqs. (8.6) and (8.7) results in:

$$\gamma_s = \frac{[\gamma_l(1 + \cos\vartheta) + \pi_{eq}]^2}{4\Phi^2\gamma_l} \approx \gamma_l\frac{(1 + \cos\vartheta)^2}{4\Phi^2}$$

$$\cos\vartheta = 2\Phi\left(\frac{\gamma_s}{\gamma_l}\right)^{1/2} - 1 - \frac{\pi_{eq}}{\gamma_l} \approx 2\Phi\left(\frac{\gamma_s}{\gamma_l}\right)^{1/2} - 1$$

- How to estimate the surface tension of solid polymers

1. Measure the contact angle with the liquid with known surface tension.

2. $\gamma \approx 0.75e_{coh}^{2/3}$, where γ expressed in mJ/m^2 and e_{coh} in mJ/m^3.
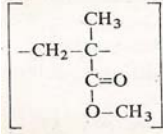
3. Using group contribution to Parachor for estimation

Example 8.1

Estimate the surface tension of solid poly(methyl methacrylate) and its contact angle with methylene iodide ($\gamma = 50.8$).

Solution

The polymeric unit is:

$$\left[\begin{array}{c} CH_3 \\ | \\ -CH_2-C- \\ | \\ C=O \\ | \\ O-CH_3 \end{array}\right]$$

From tables 8.1 and 4.6 we obtain the following group contributions to parachor and molar volume:

	P_{Si}	$V_i(cm^3)$
1(−CH₂−)	39.0	15.85
1($\overset{/}{\underset{\backslash}{C}}$)	4.8	4.6
2(−CH₃)	112.2	47.8
1(−COO−)	64.8	18.25
	220.8	86.5

So $\gamma = \left(\dfrac{P_S}{V}\right)^4 = \left(\dfrac{220.8}{86.5}\right)^4 = 2.55^4 = 42.5$.

According to eqs. (8.10) and (8.8)

$$\cos \vartheta \approx 2\Phi\left(\frac{\gamma_s}{\gamma_l}\right)^{1/2} - 1$$

$$\Phi = \frac{4(V_s V_l)^{1/3}}{(V_s^{1/3} + V_l^{1/3})^2}.$$

As calculated above, $V_s = 86.5$. For methylene iodide, $M = 267.9$ and $\rho = 3.33$, so that $V_l = 80.6$. With these values for V_s and V_l, $\Phi = 1.00$. For the contact angle with methylene iodide we find:

$$\cos \vartheta \approx 2\left(\frac{\gamma_s}{\gamma_l}\right)^{1/2} - 1 \approx 2\left(\frac{42.5}{50.8}\right)^{1/2} - 1 = 0.83.$$

so that $\vartheta \approx 34°$. The adhesion tension of methylene iodide on poly(methyl methacrylate) will be

$$\gamma_l \cos \vartheta = 50.8 \times 0.83 \approx 42 \text{ mJ/cm}^2$$

GENERAL EXPRESSION FOR THE INTERFACIAL TENSION

Expression (8.7) may be generalized to read:

$$\gamma_{12} = \gamma_1 + \gamma_2 - 2\Phi(\gamma_1\gamma_2)^{1/2} \tag{8.12}$$

or

$$\gamma_{12} \approx (\gamma_1^{1/2} - \gamma_2^{1/2})^2 \tag{8.12a}$$

since $\Phi \approx 1$. This equation, however, is only valid for substances without hydrogen bonds, as was demonstrated by Fowkes (1964).

$$\gamma = \gamma^d + \gamma^h \tag{8.13}$$

where the superscripts d and h refer to dispersion and hydrogen bonding force components. Following this suggestion, Owens and Wendt (1969) proposed the following general form of the expression for the interfacial tension:

$$\gamma_{12} = \gamma_1 + \gamma_2 - 2(\gamma_1^d \gamma_2^d)^{1/2} - 2(\gamma_1^h \gamma_2^h)^{1/2} \tag{8.14}$$

or

$$\gamma_{12} = [(\gamma_1^d)^{1/2} - (\gamma_2^d)^{1/2}]^2 + [(\gamma_1^h)^{1/2} - (\gamma_2^h)^{1/2}]^2 \tag{8.14a}$$

Substances 1 and 2 may either be liquids, or solids, or they may be a combination of a solid and a liquid.

If 1 and 2 are immiscible liquids of which γ_1 and γ_2 are known, and of which one is apolar ($\gamma^h = 0$), the γ-components of both liquids may be derived in the following way: the interfacial tension γ_{12} is measured by one of the available methods and the equations (8.14) and (8.13) are solved. In this way several liquids have been investigated; the values of γ_1, γ_1^d and γ_1^h are given in table 8.3.

Example 8.2

Estimate γ^d and γ^h of water if the following data are given:
   a. $\gamma_{H_2O} = 72.8 \text{ mJ/m}^2$ (at $20°C$)
   b. the interfacial tension cyclohexane/water is 50.2 (at $20°C$)
   c. $\gamma_{cyclohexane} = 25.5$

Solution

For cyclohexane $\gamma_{ch}^h = 0$, so that $\gamma_{ch}^d = \gamma_{ch} = 25.5$. From eq. (8.14) we get:

$$\gamma_{12} = \gamma_{H_2O,ch} = 50.2 = 25.5 + 72.8 - 2(25.5\gamma_{H_2O}^d)^{1/2}$$

from which $\gamma_{H_2O}^d = 22.7$, so that $\gamma_{H_2O}^h = 72.8 - 22.7 = 50.1$ which is in fair agreement with the most reliable values $\gamma_{H_2O}^d = 21.8$ and $\gamma_{H_2O}^h = 51.0$

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TABLE 8.3

Force components of surface tension of several liquids (after Fowkes (1964) and Owens and Wendt (1969)) (γ in mJ/m^2)

Liquid	γ_l	γ_l^d	γ_l^h
n-hexane	18.4	18.4	0
dimethyl siloxane	19.0	16.9	2.1
cyclohexane	25.5	25.5	0
decalin	29.9	29.9	0
bromobenzene	36.3	36.0	≈ 0
tricresyl phosphate	40.9	39.2 ± 4	≈ 1
aniline	42.9	24.2	18.7
α-bromonaphthalene	44.6	47 ± 7	≈ 0
trichlorobiphenyl	45.3	44 ± 6	≈ 1.3
glycol	48.0	33.8	14.2
methylene iodide	50.8	49.5 ± 1	≈ 1.3
formamide	58.2	39.5 ± 7	≈ 19
glycerol	63.4	37.0 ± 4	≈ 26
water	72.8	21.8 ± 0.7	51

Owens and Wendt also gave a more general expression for (8.10), viz.:

$$1 + \cos \vartheta \approx 2\left[\frac{(\gamma_s^d)^{1/2}(\gamma_l^d)^{1/2}}{\gamma_1} + \frac{(\gamma_s^h)^{1/2}(\gamma_l^h)^{1/2}}{\gamma_1}\right]. \qquad (8.15)$$

This equation permits the derivation of γ_s^d and γ_s^h via measurements of the contact angles ϑ of two liquids if γ_l and γ_l^d and γ_l^h of both liquids are known.

Example 8.3

Estimate γ_s and its components γ_s^d and γ_s^h for poly(vinyl chloride) if the following data are known:

a. for water: $\gamma_{H_2O} = 72.8$; $\gamma_{H_2O}^d = 21.8$; $\gamma_{H_2O}^h = 51.0$

b. for methylene iodide: $\gamma_{mi} = 50.8$; $\gamma_{mi}^d = 49.5$; $\gamma_{mi}^h = 1.3$

c. for the contact angles on PVC: $\vartheta_{H_2O} = 87°$; $\vartheta_{mi} = 36°$

Solution

Substitution of the data in eq. (8.15) gives:

for water:

$$1 + 0.052 = 2\left[\frac{(\gamma_s^d)^{1/2}21.8^{1/2}}{72.8} + \frac{(\gamma_s^h)^{1/2}51.0^{1/2}}{72.8}\right]$$

for methylene iodide:

$$1 + 0.809 = 2\left[\frac{(\gamma_s^d)^{1/2}49.5^{1/2}}{50.8} + \frac{(\gamma_s^h)^{1/2}1.3^{1/2}}{50.8}\right]$$

Solution of these simultaneous equations gives:

$$\gamma_s^d = 40.0; \gamma_s^h = 1.5; \gamma_s = 41.5.$$

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TABLE 8.4

Components of surface energy for various solid polymers (Owens and Wendt, 1969) (γ in mJ/m^2)

Polymer	γ_s^d	γ_s^h	γ_s	γ_{cr}
polyethylene (l.d.)	33.2	0.0	33.2	31
polystyrene	41.4	0.6	42.0	43
poly(vinyl chloride)	40.0	1.5	41.5	39
poly(vinylidene chloride)	42.0	3.0	45.0	40
poly(vinyl fluoride)	31.3	5.4	36.7	28
poly(vinylidene fluoride)	23.2	7.1	30.3	25
poly(trifluoroethylene)	19.9	4.0	23.9	22
poly(tetrafluoroethylene)	18.6	0.5	19.1	18.5
poly(methyl methacrylate)	35.9	4.3	40.2	39
poly(ethylene terephthalate)	43.2	4.1	47.3	43
nylon 6,6	40.8	6.2	47.0	46

VI. Transport properties (Diffusion)

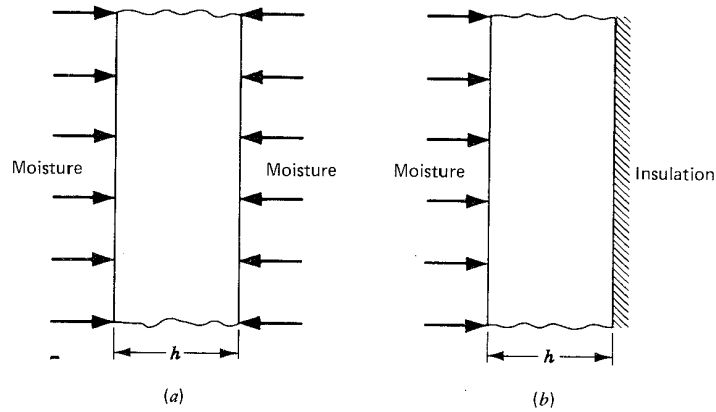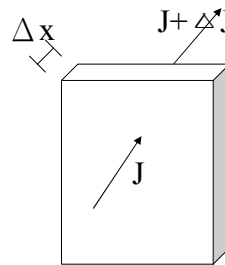**Figure 3.38.** Description of problem of diffusion in a plate.

From the Fick's first law

the flux $J = -D\dfrac{\partial c}{\partial x}$

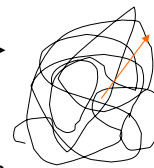$\lim\limits_{\Delta x \to 0} \dfrac{J - J - \Delta J}{\Delta x} = \dfrac{\partial c}{\partial t}$

So, $\dfrac{\partial c}{\partial t} = \dfrac{\partial}{\partial x} D \dfrac{\partial c}{\partial x}$ (Fick's second law)

If D is independent of c and x, $\dfrac{\partial c}{\partial t} = D \dfrac{\partial^2 c}{\partial x^2}$

$R = nl \longrightarrow \overline{S^2} = \dfrac{nl^2}{6}$

If $u = \phi_o l$, $D = \dfrac{\phi_o l^2}{6}$ where Φ_o is the jump frequency

B.C. C=C$_i$ for 0<x<h at t≤0 and C=C$_m$ at x=0, x=h , and t>0

By using the separation method, we can obtain

$$\frac{c-c_i}{c_m-c_i}=1-\frac{4}{\pi}\sum_{j=0}^{\infty}\frac{1}{2j+1}\sin\frac{(2j+1)\pi x}{h}\exp\left[\frac{-(2j+1)^2\pi^2Dt}{h^2}\right]$$

Let $m=A\int_0^h cdx$, where A is the conversion factor

$$G=\frac{m_t-m_i}{m_m-m_i}=1-\frac{8}{\pi^2}\sum_{j=0}^{\infty}\frac{\exp\left[-(2j+1)^2\pi^2(Dt/h^2)\right]}{(2j+1)^2}$$

In the environment test, M%=[(weight of moist sample-weight of dry sample)/weight of dry sample]x100%=

$$\frac{W-W_d}{W_d}\times100\%=\frac{m}{W_d}\times100\%\quad,\quad G=\frac{M_t-M_i}{M_m-M_i}$$
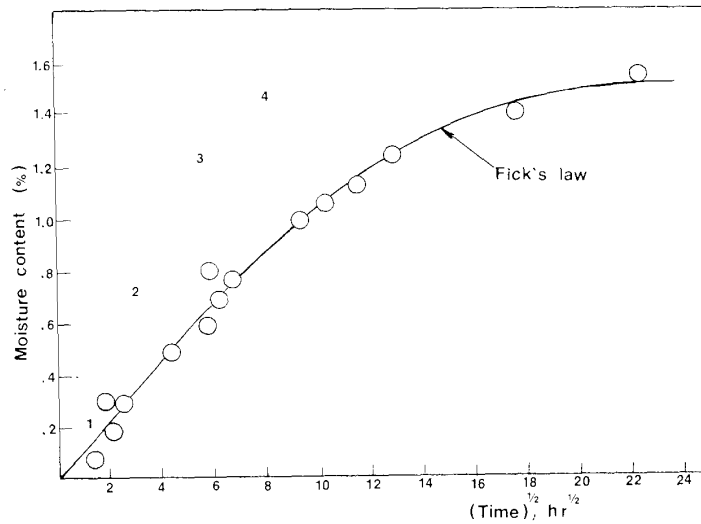
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Figure 3.   *Moisture content as a function of square root of time of exposure to 90 °C/100% RH. Note four (1–4) stages of moisture absorption.*

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- For the specimens with an infinitive thickness

$$\frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2}$$

B. C. $C=C_i$ for $0<x<\infty$ at $t\leq 0$

and $C=C_m$ at $x=0$, and $t>0$

$$\frac{C_t - C_i}{C_m - C_i} = 1 - erf \frac{x}{2\sqrt{t}}$$

$$m = -A \int_0^t D_x \left(\frac{\partial C}{\partial x} \right)_{x=0} dt = 2A(C_m - C_i)\sqrt{\frac{Dt}{\pi}}$$

- Since $M\% = \dfrac{W - W_d}{W_d} \times 100\% = \dfrac{m}{W_d}\%$,

for the initial stage of moisture absorption

$$M = \frac{4M_m}{h\sqrt{\pi}} \sqrt{D}\sqrt{t} \ , \ D = \left(\frac{M_2 - M_1}{\sqrt{t_2} - \sqrt{t_1}} \right)^2 \left(\frac{h\sqrt{\pi}}{4M_m} \right)^2$$

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- For the three dimensional consideration,

$$\frac{dC}{dt} = D_x \frac{\partial^2 C}{\partial x^2} + D_y \frac{\partial^2 C}{\partial y^2} + D_z \frac{\partial^2 C}{\partial z^2}$$

$$G = \frac{M_t - M_i}{M_m - M_i} = 1 - \frac{8}{\pi^2} \left\{ \left(1 - \frac{4\sqrt{Dt}}{\sqrt{\pi l^2}} \right) \left(1 - \frac{4\sqrt{Dt}}{\sqrt{\pi n^2}} \right) \sum_{i=0}^{\infty} \frac{1}{(2i+1)^2} \exp\left[-(2i+1)^2 \frac{\pi^2 Dt}{h^2} \right] \right\}$$

In the initial stage of moisture absorption,

$$m = 4(C_m - C_i)(nl\sqrt{D_x} + nh\sqrt{D_y} + hl\sqrt{D_z})\sqrt{\frac{t}{\pi}}$$

$$M = \frac{4M_m}{h\sqrt{\pi}} \left(\sqrt{D_x} + \frac{h}{l}\sqrt{D_y} + \frac{h}{n}\sqrt{D_z} \right)\sqrt{t}$$
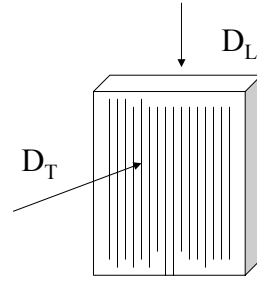
$$= \frac{4M_m}{h\sqrt{\pi}} \sqrt{D}\sqrt{t}$$

If $D_x = D_y = D_z$

where $D = D_x(1 + \frac{h}{l}\sqrt{\frac{D_y}{D_x}} + \frac{h}{n}\sqrt{\frac{D_z}{D_x}})^2$ $\qquad D = D_x\left(1 + \frac{h}{l} + \frac{h}{n}\right)^2$

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For the unidirectional composites,

$D_L = (1-V_f)D_m + V_f D_f^{\nearrow 0}$

D_L

D_T

$$D_T = \left(1 - 2\sqrt{V_f/\pi}\right)D_m + \frac{D_m}{B_D}\left[\pi - \frac{4}{\sqrt{1-\left(B_D{}^2 V_f/\pi\right)}}\tan^{-1}\frac{\sqrt{1-(B_D{}^2 V_f/\pi)}}{1+B_D\sqrt{V_f/\pi}}\right]$$

where $B_D = 2\left(\dfrac{D_m}{D_f}-1\right)$. When $D_f \longrightarrow 0$, $D_T \cong \left(1 - 2\sqrt{V_f/\pi}\right)D_m$

Since $D_T = D_x = D_y$, $D_L = D_z$

$$D = D_T\left(1 + \frac{h}{l} + \frac{h}{n}\sqrt{\frac{1-V_f}{1-2\sqrt{V_f/\pi}}}\right)^2$$

From the slope of experimental data, we can obtain D, D_T, D_m and D_L.

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