

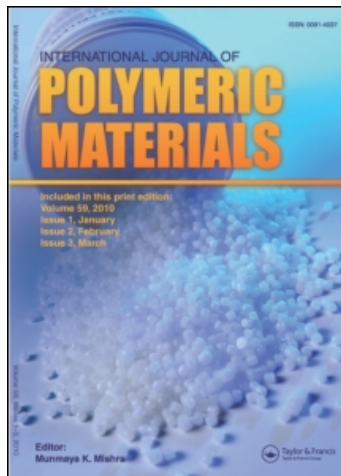
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Publisher *Taylor & Francis*

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## International Journal of Polymeric Materials

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713647664>

## About the Polymer Free Volume Theory

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**To cite this Article** Nechitailo, V. S.(1992) 'About the Polymer Free Volume Theory', International Journal of Polymeric Materials, 16: 1, 171 – 177

**To link to this Article:** DOI: 10.1080/00914039208035420

**URL:** <http://dx.doi.org/10.1080/00914039208035420>

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## About the Polymer Free Volume Theory

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The fluctuation-dissipation theory of free volume in condensed media is discussed. The free volume concept developed is applicable in the theory of viscoelastic properties and thermal expansion of polymers.

KEY WORDS Free volume, polymers, theory.

### THEORETICAL DISCUSSION

The free volume concept in condensed media proves to be very useful and applicable for a theoretical description of many processes occurring in liquids and polymers. It serves as a basis for developing the theories of polymer low molecular weight compound diffusion, of polymer thermal conductivity, solubility, and so forth (see Reference 1 and references to it). In particular, the thermal expansion coefficient for liquids and polymers is mostly due to a higher free volume.<sup>2</sup>

The free volume concept finds the widest use in the polymer viscoelastic property theory developed by Williams, Landell and Ferri (WLF)<sup>2</sup> on the basis of the Doolittle empirical equation,<sup>3</sup> involving the viscosity  $\eta$  and the specific free volume  $f$  through the ratio:

$$\eta(T) = a \exp(b/f), \quad (1)$$

where  $a$  and  $b$  are constants,

$$f = \frac{V - V_o}{V} = \frac{V_f}{V}, \quad (2)$$

$V$ ,  $V_o$ ,  $V_f$  are the real, occupied, and free volumes of a medium at temperature  $T$ . According to this theory, changes in the viscosity and relaxation time of structural

units of the medium  $\tau$  at the temperature range of from  $T_g$  to  $T$  may be described by using the reduction coefficient in agreement with the WLF equation:<sup>2</sup>

$$\begin{aligned} \lg \alpha_T &= \lg \frac{\tau(T)}{\tau(T_g)} = \lg \frac{\eta(T)}{\eta(T_g)} = \frac{C_1(T - T_g)}{C_2 + (T - T_g)} \\ &= \frac{-(b/2,3 f(T_g))(T - T_g)}{f(T_g)d_f + (T - T_g)}, \end{aligned} \quad (3)$$

where  $T_g$  is the structural glass-transition temperature dilatometrically determined and  $C_1$  and  $C_2$  are the "universal" constants:

$$C_1 = \frac{b}{2,3 f(T_g)} = 17.4, \quad C_2 = \frac{f(T_g)}{d_f} = 51.6 \quad (4)$$

and  $d_f$  is the temperature coefficient of free volume changes:

$$f(T) = f(T_g) + d_f(T - T_g). \quad (5)$$

Proceeding from the "universal"  $C_1$  and  $C_2$  constant values found and assuming that  $b = 1$  (in accordance with the results by Doolittle) Williams, Landell and Ferri obtain

$$f(T_g) = 0.025 \quad \text{and} \quad d_f = 4.8 \cdot 10^{-4} \text{ grad}^{-1}. \quad (6)$$

While deriving equation (3), it is assumed that the free volume depends linearly on  $T$  (see (5)), though the dependence<sup>4,5</sup>

$$f(T) \sim T^{3/2} \quad (7)$$

is observed experimentally. It should be noted that multiple attempts to substantiate the dependence (7) (see, e.g., reference 5) theoretically have failed.

An indefinite value of the  $T_g$  temperature is used, whose value depends on various factors (a cooling rate, the presence of residual monomer and moisture), so it is concluded that the fraction of the free volume at the glass-transition temperature  $f(T_g) = \text{const.}$  (see (6)) is not correct for all polymers. Moreover, as is noted in reference 1,  $f(T_g)$  depends on the flexibility of the polymer chain, the pattern of molecular packing, and the method for assessing the occupied volume, as the fraction of the free volume is determined by the equation (2).

The latter fact itself contains some known uncertainty of the physical meaning of free volume and so the values of  $f(T_g)$  calculated by various methods in accordance with various free volume theories<sup>1,2,5,6</sup> are inconsistent. Thus, the fraction of free volume  $f(T_g)$  is 0.025 (see (6)), if calculated using the WLF equation (3), whereas it is 0.1–0.15, if calculated using the data on compressibility or using the assumption of volume additivity for various atomic groups.<sup>7</sup>

All of this suggests that the polymer free volume theory is far from complete

and requires new concepts to be developed and new parameters of respective states to be obtained for adequate description of viscoelastic properties and many processes (see above) in liquids and polymers.

Let us consider the following model of a condensed medium. Let it consist of structural elements having mass  $m$  and let the element be disturbed from equilibrium for the  $x_0$ -value at initial time  $t = 0$ . Then at  $t > 0$ , it restores the equilibrium according to the following equation:

$$\ddot{x} + 2\delta \dot{x} + w_0^2 x = 0, \quad (8)$$

where  $\delta \equiv z/m$ ,  $w_0^2 \equiv K/m$ , and  $K$  and  $z$  are the coefficients of elasticity and friction, respectively. In the case where  $\delta < w_0$  ( $z < \sqrt{Km}$ ), the element makes damped vibrations with its inherent fall time  $\tau_d = 1/\delta$ , and the less they are, the higher the  $z$  friction coefficients. With  $\delta = \delta_0 = w_0$ , the motion of the element becomes aperiodic (nonoscillatory) with the minimal relaxation time

$$\tau_0 = \frac{1}{\delta_0} = \frac{1}{w_0} = \frac{m}{z_0} = \sqrt{\frac{m}{K}} \quad (9)$$

at the friction coefficient  $z_0 = \sqrt{Km}$ .<sup>†</sup> With  $\delta > w_0$  ( $z > z_0$ ), the motion of the element (relaxant) occurs with two relaxation times: "short,"

$$\tau_1 = \tau_0 \frac{w_0/\delta}{1 + \sqrt{1 - w_0^2/\delta^2}} < \tau_0$$

and "long,"  $\tau$ , which has the physical meaning

$$\tau = \tau_0 \frac{w_0/\delta}{1 - \sqrt{1 - w_0^2/\delta^2}} > \tau_0. \quad (10)$$

For polymers, at  $\delta \gg w_0$  ( $z \gg z_0$ ) it is easy to obtain, from (10),

$$\tau = \frac{2z}{K} = 2\tau_0 \frac{z}{z_0} = 2\tau\eta/\eta_0 \gg \tau_0, \quad (11)$$

from which, taking into account (1) at  $a = \eta_0/2$ ,  $b = 1$ , we finally obtain

$$\tau = \tau_0 \exp(1/f). \quad (12)$$

Let the structural element in the medium with  $z \gg z_0$  (relaxant) be affected by the periodic force with amplitude  $f_0$ , frequency  $w \ll w_0$  and  $\hbar w \ll K_B T$ , and  $\hbar$

<sup>†</sup>The value shows that the medium viscosity  $\eta_0 = 10^{-3} - 10^{-4}$  (g/s·cm) corresponds to the friction coefficient  $z_0$ , whereas  $\eta \geq 10^{-2}$  (g/s·cm), for most liquids.

and  $K_B$  are the Planck and Boltzmann constants, respectively. The energy dissipated by the relaxant for the period is

$$Q = \frac{\pi}{2K} \frac{2w\tau}{1 + w^2\tau^2} f_0^2. \quad (13)$$

From (13) it can easily be seen that the maximum consumed energy occurs at

$$w = w_m = \frac{1}{\tau(T)} = \frac{K}{2z(T)} \quad (14)$$

and makes up

$$Q = Q_m = \pi f_0^2 / 2K, \quad (15)$$

the absorption band  $Q/Q_m(lgw)$  being symmetrical with its width at the semiheight

$$\Delta = lgw_1 - lgw_2 = lg \frac{2 + \sqrt{3}}{2 - \sqrt{3}} = 1.14. \quad (16)$$

With the analysis of the values obtained for the relaxant, a structural element in question indicates that the following situation which is important for it occurs, namely: changes in the medium temperature lead to those in the relaxation of the element by (14) (due to modification of the coefficient  $z(T)$ ), only a shift of the maximum absorption band being seen on the axis  $lgw$  in accordance with (14), but the intensity of the absorption band and its width do not depend on  $T$  (see (15) and (16)). Thus, the relaxant absorption of energy does not depend on the viscosity of a medium and its temperature and is determined by the elasticity coefficient alone.

Now let us consider fluctuations of a one-dimensional relaxant. According to the fluctuation-dissipation theorem,<sup>8</sup> involving the fluctuation of physical quantities and the dissipative properties of the system externally affected, we shall find the mean-square value of the fluctuation deviation of the relaxant from the equilibrium

$$\bar{x}^2 = \frac{2K_B T}{\pi} \int_0^\infty \frac{d''(w)}{w} dw, \quad (17)$$

where the imaginary fraction of the total susceptibility of the relaxant is

$$d''(w) = \frac{1}{K} \frac{w\tau}{1 + w^2\tau^2}. \quad (18)$$

Substituting (18) into (17), we get

$$\bar{x}^2 = \frac{K_B T}{K}. \quad (19)$$

It is evident that the mean-square value of the fluctuation deviation of the relaxant does not depend on the viscosity of a medium and is determined by the thermal energy  $K_B T$  and the elasticity coefficient  $K$ .

The probability distribution for various fluctuation  $x$ -values is determined by<sup>8</sup>

$$w(x)dx = \frac{1}{\sqrt{2\pi\bar{x}^2}} \exp\left(-\frac{x^2}{2\bar{x}^2}\right) dx. \quad (20)$$

a distribution of this kind is called a Gaussian distribution.

In the case of a three-dimensional relaxant (which is a structural element of a medium), the mean square values of fluctuation deviations  $\bar{y}^2$  and  $\bar{z}^2$  are found in the same manner as in (19), in general, by different values of the elasticity coefficient ( $K_x, K_y, K_z$ ). The distribution of probabilities  $w(x, y, z)dxdydz$  for the three statistically independent values  $X, Y$  and  $Z$  is the product of three independent Gaussian distributions for the  $X, Y$  and  $Z$  values:

$$w(x, y, z)dxdydz = w(x) \cdot w(y) \cdot w(z)dxdydz. \quad (21)$$

Based on the found mean-square values of fluctuation deviations  $\bar{X}^2, \bar{Y}^2$  and  $\bar{Z}^2$ , the mean-square value of the fluctuation volume of a relaxant can be determined:

$$v_f = 8\sqrt{\bar{x}^2 \cdot \bar{y}^2 \cdot \bar{z}^2} = 8 \frac{(K_B T)^{3/2}}{(K_x \cdot K_y \cdot K_z)^{1/2}} = \left(\frac{4K_B T}{K_m}\right)^{3/2} \quad (22)$$

where the average elasticity coefficient is  $K_m = \sqrt[3]{K_x \cdot K_y \cdot K_z}$ . The probability distribution is determined for various values of fluctuation volume (21).

Thus, the free volume we have found in a polymer

$$V_f = Nv_f, \quad (23)$$

where  $N$  is the number of relaxants, is virtually a fluctuation volume and is determined by the thermal energy and elasticity coefficient for a structural medium element, rather than the real-occupied volume difference, as previously supposed (see (2)). So, to find the free volume within the scope of the theory developed by us, there is no need to know the well indefinite volume.

As seen from (22) and (23), the free volume depends on the temperature

$$V_f \sim T^{3/2} \quad (24)$$

in full accord with the experimental results,<sup>4,5</sup> which is the important reason for the developed concepts of polymers.

Let us use the developed free volume concept in the theory of polymer viscoelastic properties. Taking into account the assumption given in reference 9, that the structural element can migrate when the proportion of the locally relative free

volume  $f_s$  exceeds some critical value  $f_c$ , for relaxation time, we have the following, from (12):

$$\tau = \tau_0 \exp \left( \frac{1}{f_s - f_c} \right), \quad (25)$$

where

$$f_s = \frac{V_f}{V_s} = \frac{1}{V_s} \left( \frac{4K_B T}{K_m} \right)^{3/2}, \quad f_c = \frac{1}{V_s} \left( \frac{4K_B T_0}{K_m} \right)^{3/2} \quad (26)$$

and  $V_s$  is the real volume of the structural element,  $T_0$  is the temperature being below the  $T_g$  of a polymer and determined from the condition  $\tau \rightarrow \infty$  at  $T \rightarrow T_0$ . Substituting (26) into (25), we finally get

$$\tau = \tau_0 \exp \left[ \frac{V_s}{\left( \frac{4K_B T}{K_m} \right)^{3/2} - \left( \frac{4K_B T_0}{K_m} \right)^{3/2}} \right]. \quad (27)$$

The change in the relaxation time of structural elements at a temperature range of from  $T_g$  to  $T$  may be described by

$$\lg \alpha_T = \lg \frac{\tau(T)}{\tau(T_g)} = \frac{V_s/2,3}{\left( \frac{4K_B T_g}{K_m} \right)^{3/2} - \left( \frac{4K_B T_0}{K_m} \right)^{3/2}} \cdot \frac{T^{3/2} - T_g^{3/2}}{T^{3/2} - T_0^{3/2}}, \quad (28)$$

which at  $T - T_g \ll T_g$  can be presented as

$$\lg \alpha_T = - \frac{V_s/2,3}{\left( \frac{4K_B T_g}{K_m} \right)^{3/2} - \left( \frac{4K_B T_0}{K_m} \right)^{3/2}} \cdot \frac{T - T_g}{\frac{2}{3} T_g \left[ 1 - \left( \frac{T_0}{T_g} \right) \right]^{3/2} + (T - T_g)}, \quad (29)$$

which is similar to the WLF equation (3).

Proceeding from (29) with regard to the empirically found values of the "universal" constants  $C_1$  and  $C_2$  (see (4)), we find the values of  $K_m$  and  $T_0$  for segments in poly(methyl methacrylate), which consist of seven monomeric units at  $V_s = 977.5 \cdot 10^{-24} \text{ cm}^3$  and  $T_g = 383 \text{ K}$ . Equating

$$\frac{2}{3} T_g \left[ 1 - \left( \frac{T_0}{T_g} \right)^{3/2} \right] = C_2 = 51.6, \quad (30)$$

we get  $T_0 = 329.4 \text{ K}$ , which is 53.6 K lower than  $T_g$  and in good agreement with

$T_0 = 329.4$  K presented in reference 2. With allowance made for the  $T_0$  value found from (27) and

$$\frac{V_s/2,3}{\left(\frac{4K_B T_g}{K_m}\right)^{3/2} - \left(\frac{4K_B T_0}{K_m}\right)^{3/2}} = C_1 = 17.4, \quad (31)$$

we find  $K_m = 86.5$  dn/cm and  $\tau_0 = 3.67 \cdot 10^{-12}$  sec.

The  $K_m$  and  $T_0$  values found allow us to find the specific free volume in a polymer at  $T_g$ ,

$$f(T_g) = \frac{1}{V_s} \left(\frac{4K_B T_g}{K_m}\right)^{3/2} = 0.124, \quad (32)$$

which is, as in the literature, determined from the data on compressibility,<sup>7</sup> and the specific available fluctuation volume

$$f(T_g) - f(T_0) = 0.025, \quad (33)$$

which is determined from the data on the viscoelastic (relaxation) characteristics of a polymer, as shown by the literature. It is easy to obtain  $d_f = 4.86 \cdot 10^{-4}$  grad<sup>-1</sup> from (26).

Given that  $\tau(T_1) = 1$  sec. with regard to (27), we find that  $T_1 = 410$  K, which is in good agreement with the value of  $T_1 = 413$  K given in reference 2. Determining  $T_2$  from the condition  $\tau(T_2) = 0.1$  sec, it is easy to show that  $T_2 - T_1 \approx 7$  K, which coincides with the value experimentally measured.

Thus, this paper develops a new concept in the free volume theory in polymers and introduces new parameters for respective conditions, which enable the viscoelastic properties and other properties to be adequately described in liquids and polymers.

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