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RELAXATION TIME OF PVAc AS A FUNCTION OF HOLE FRACTION COMPUTED FROM SIMHA-SOMCYNSKY THEORY

ASEEL ALMASHAYEK

(521220992)

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Department of Physics

Thesis Supervisor

Prof. Dr. Uğur YAHŞİ

Thesis Co-supervisor

Prof. Ayşe YUMAK YAHŞİ

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FEN BİLİMLERİ ENSTİTÜSÜ

SIMHA-SOMCYNSKY TEORİSİNDEN HESAPLANAN BOŞLUK KESRİNİN BİR FONKSİYONU OLARAK PVAc'NİN RELAKSASYON ZAMANI

ASEEL ALMASHAYEK

(521220992)

YÜKSEK LİSANS TEZİ

Fen Bilimleri Enstitüsü

DANIŞMAN

Prof. Dr. Uğur YAHŞİ

EŞ-DANIŞMAN

Prof. Ayşe YUMAK YAHŞİ

İSTANBUL, 2023

Preface

“Allah raises the ranks of those among you who believe and those who were granted the knowledge” from the Holy Quran, Surat Az-Zumar, Ayah 9

My endless thanks to the creator, Allah, for his support and giving throughout my whole life and for completing this thesis.

The first lines of my thesis are dedicated to those who are very important to me and who have supported, encouraged, and blessed me throughout my long-term studies.

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I would like to express my sincere gratitude to my beloved husband Ahmad as well as my children, Yaseen and Leen for their constant support and encouragement.

I would not be able to accomplish any of this without this love and support.

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ÖZET

SIMHA-SOMCYNSKY TEORİSİNDEN HESAPLANAN BOŞLUK KESRİNİN BİR FONKSİYONU OLARAK PVAc'NİN RELAKSASYON ZAMANI

Polimerlerin gevşeme davranışı ile ilgili (sıcaklık ve basınç) değişimler arasındaki korelasyon, makromoleküllerin türlerine, şekillerine ve yeni mimarilerle gerekli olan bir dizi dala dayanan istatistiksel termodinamiği üzerine araştırma alanının devamıdır.

Çalışmamızda iki teoriyi birbirine takıyoruz: Denge teorisi olarak Simha-Somcynsky Delik Teorisi ve taşıma teorisi olarak Eyring Önemli Yapı Teorisi. Her iki teori de polimerlerin gevşeme süresini bir taşıma fenomeni olarak yorumlamak için özetlenmiş ve birleştirilmiştir. bazı polimerleri, belirli bir basınç ve sıcaklık aralığında ölçülen belirli yoğunluk ve gevşeme süresindeki mevcut verilerle birlikte kullanacağız.

polimerlerin gevşeme süresini, Eyring Önemli Yapı (ESS) taşıma teorisi ve Simha-somcyncky ile ilgili bir taşıma fenomeni olarak yorumlamak için teorik bir model geliştirdik ve PVAc'nin (Polipropilen glikol) moleküler ağırlıklı poli vinilasetatPVAc'nin (Mw = 93080 kg mol-1) gevşeme süresini, çeşitli sıcaklıklarda ve yüksek basınçlarda delik fraksiyonunun bir fonksiyonu olarak araştırdık. Zincir moleküllerinin yapısal gevşeme davranışına dayanan bu model, sıcaklık ve sıcaklığa bağlı delik fraksiyonu açısından "termo-doluluk" fonksiyonu ile tartışılmış ve serbest hacim modeli ile karşılaştırılmıştır.

Ve sonra, gevşeme logaritmasının türevini delik fraksiyonu ile ilgili olarak keşfedin, gevşeme fraksiyonu değişimi ile beklenen şekilde keskin bir şekilde azalır veya artar, gevşetilebilirlik (gevşeme ve delik fraksiyonundan türetilmiştir) olarak adlandırılır.

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ABSTRACT

RELAXATION TIME OF PVAc IN TERMS OF HOLE FRACTION COMPUTED FROM SIMHA-SOMCYNSKY THEORY

The correlation between the relaxation behavior of polymers and the related temperature and pressure changes is the sequel to the research area on the statistical thermodynamics of macromolecules based on their type, shape, and a number of branches that have been essential with new architectures.

In our study, we bridge two theories: Simha-Somcynsky hole theory as equilibrium theory and Eyring significant structure theory as transport theory. We interpret transport phenomena such as the relaxation time in terms of the hole fraction, which is a measure of the free volume as an equilibrium property. We will employ PVAc (poly vinyl acetate) (Mw = 93 080 g/mol^{-1}) with the available data in specific volume and relaxation time measured in some range of temperature and pressure. We have employed a theoretical model recently proposed for the relaxation time of polymers using the transport theory of Eyring Significant Structure (ESS) and the equilibrium theory of Simha-Somcynsky. An analysis of the structural relaxation of chain molecules as determined by the 'thermo-occupancy' function is presented and compared with the free volume model based on the temperature and temperature–pressure dependence of the hole fraction. Our study examines the relaxation time of PVAc as a function of the hole fraction at different temperatures and pressures. In addition to discussing the logarithm of relaxation with respect to the hole fraction, we have also discussed relaxiholibility (derived from relaxation and hole fraction), which is expected to decrease or increase as the hole fraction changes.

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SYMBOLS

B	:	Number of bonds in the polymer chain
C	:	Degree of freedom
C	:	Carbon atom
D_B	:	Diagrams of B bond vector
g	:	Combinational factor
h	:	Hole fraction
K	:	Temperature unit (Kelvin)
m_i	:	Segmental mass of the i^{th} molecule (kg)
m_0	:	Segmental mass (kg)
N	:	Number of molecules
N_b	:	Number of free sites
N_l	:	Number of lattice sites
ϕ_1	:	The volume fraction of solvent
ϕ_2	:	The volume fraction of solute
P	:	Pressure (Pa)
$\tilde{P},\tilde{V},\tilde{T}$	:	Reduced Pressure, Volume, Temperature
P^*,V^* T^*,ε^*	:	Characteristic parameters (Pa, m^3/kg, K, K)
Ψ_{conf}	:	Configurational partition function
Z_{conf}	:	Configurational partition function according to SS

Q	:	Partition function of normal segment
q	:	Bond vector between segments
q_z	:	The bond vector formed by the s-mer nearest neighbor molecules
r	:	Distance from the cell center of the molecule (m)
$\vec{r}$	:	Position vector
s	:	Number of segments of a molecule
s_i	:	Segment number for the i^{th} molecule
S	:	Entropy (J/K)
S_{conf}	:	Configurational entropy (J/K)
T	:	Temperature (K)
U	:	Potential energy (J)
V^0	:	Molecular volume (m^3/kg)
V	:	Total volume
υ	:	Molar segmental volume (m^3/mole)
υ_f	:	Free volume (m^3/mole)
υ^0	:	Molecular volume for $r = \sigma$ (m^3/mole)
y	:	Volume fraction
w	:	Number of possible states
Ω_{i+1}	:	The number of placement options is the i^{th} molecule
Z	:	Number of nearest neighboring sites
γ_D	:	Combinatorial coefficient associated with nonzero vectors in each diagram
ε	:	Interaction energy between molecular pairs (k. K)
σ	:	Segment radius (m)
$\omega(r)$	:	Average energy of neighboring interactions (J)

$\delta_{r_i,r_j} = \delta_{i,j}$: Dirac-delta

UNIVERSAL CONSTANT

N_A : Avogadro number $(6.02\times10^{23}\ \text{mol}^{-1})$

R : Ideal gas constant $(8.314\ J/mol.K^o)$

K : Boltzmann constant $(1.38\times10^{-23}\ J/K^o)$ $1.38\times10^{-23}\ J/K^o$

ABBREVIATIONS

FHMF: Flory-Huggins Mean Field Theory

LTC : Lattice Cluster Theory

Mw : Molecular Weight

NRM : Newton Raphson Method

PIMT : Pseudo Inverse Matrix Technique

SS : Simha-Somcynsky Theory

PVAc : Polyvinyl Acetate

VFT : Vogel–Fulcher–Tammann equation

PEAG: Pressure-extended Adam–Gibbs equation

DLLs : Dynamic Lattice Liquids

PALS : Positron Annihilation Lifetime Spectroscopy

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1. INTRODUCTION AND PURPOSE

When a force is applied to polymers, the relaxation time indicates how quickly they reach equilibrium. By moving the polymer to fill any gaps, the material is in equilibrium as a result of removing a deformation in the polymer mesh.

Thermal fluctuations in the material can cause polymer chains to move inside the material. These movements can occur in a variety of ways. The polymers can be rotated, translated, or stretched through the net. Due to thermal fluctuations, the directions and speed of these movements are random. Their ability to move varies depending on factors such as their packing, weight, entanglement, and polar interactions.

It is difficult to describe the movement of polymers with a single number, so we use relaxation time to describe the movement. This investigation of the temperature–pressure dependence of the relaxation time via the dielectric spectroscopy technique has been extensively studied. [1-6] Additionally, the Vogel-Fulcher (VF) form has been used to express the temperature-dependent dielectric relaxation of some polymers. $\tau = \tau_0 \exp\left(B/(T - T_0)\right)$ [7, 8], also the VFT law provides an accurate prediction of non-Arrhenius relaxation behavior in glassy and melted polymeric materials, where τ is the characteristic relaxation time, τ_0 is a referenced relaxation time, B is a constant, T_0 is the VFT temperature, and T is the absolute temperature. When $T = T_0$ is the case of linear temperature dependence, and at $T_0 = 0$ reduced to the Arrhenius relaxation dynamics case.

Several studies have investigated the pressure dependence of the VF equation as a phenomenological extension based on pressure [2-4].

Molecular rearrangements can be described by dynamic lattice liquids (DLLs) [9] By taking into account the molecular rearrangements responsible for not only temperature but also free volume, the structural relaxation behavior of polymers is explained adequately by this model, as well as an enlightening concept to explain the isothermal and isobaric dependence of structural relaxation. However, Dlubek et al. [10] investigated structural relaxation processes in some melt polymers based on the free volume theory of

Cohen and Turnbull [11, 12]. For a structural relaxation process to occur, there must be a minimum specific free volume γv_f^* and a mean specific free volume V_f, [13, 14]

Our research has also included the application of a theoretical model for interpreting polymer relaxation times in terms of Eyring Significant Structure (ESS) and Simha-Somcynsky (SS) holes [15-17], which were constructed by analyzing temperature-dependent specific volumes and dielectric relaxation measurements. [18, 19]

We will use polyvinyl acetate (PVAc) with available data on density and relaxation time. It has a set of characteristics, such as being highly branched, noncrystalline, and derived via a conventional free radical polymerization process. It is resistant to ultraviolet radiation and oxidation, although it is fairly brittle below its melting point (35°C) and very sticky above that point.

Emulsions of PVAc are produced on a large scale in industries. It is one of the core ingredients of water-based glues, such as wood glue or white glue [20, 21].

2. THEORIES

As a result of the microscopic dynamics of their constituent molecular chains, polymer liquids, also called polymer melts, have a unique flow behavior. The mechanism by which these chains move has been described by multiple theories developed over the last half-century. To explain why the dielectric relaxation of some polymers varies with temperature, various theories have been developed based on the chain flexibility of each chain, such as the Adam-Gibbs model, Vogel-Fulcher model, dynamic lattice liquid model (DLL), free volume model of Cohen and Turnbull, and many advanced theories to understand polymer solution behaviors.

2.1. The Flory-Huggins mean field theory

According to Flory Huggins mean-field theory, mixing two different chemical species has both entropic and enthalpic contributions [7, 13, 22] In this theory, molecule interactions are determined by an average interaction force involving all the molecules in the system and the interaction force of a given molecule. Each molecule occupies a site on the lattice in the mixture.

Paul Flory and Maurice Huggins conducted independent studies on polymer solutions thermodynamically in the early 1940s. Based on the equation below, a rigid lattice frame was assumed by them, a system in which molecules are distributed over N_0 lattice points in their solutions/mixtures and in pure liquids. Based on the assumption that the polymer repeat unit N_{pr} and the solvent molecule N_s are equal, we can calculate the number of lattice sites N_0 [10].

In addition to polymer-polymer solutions, this approach can handle polymer-solvent solutions. To accomplish this, we will apply Flory-Huggins, and we will use a lattice approach with a mean-field estimate similar to our regular solution theory. Through the combination of entropy and energy of mixing, a formulation will be developed for the free energy of mixing [11].

Assuming that each lattice site has the same volume, we can express the whole volume using the following expression V_o:

$$V = (sN + N_b)V_0 \tag{2.1}$$

As a result, the lattice site number N_l becomes $N_l = sN + N_b$, and the fundamental conceptual principle behind it is that N_l, the lattice sites that are occupied by molecules N, have each been assigned a segment (s), whereas N_b, the lattice sites that are not occupied by molecules, are all left free. Using this criterion, we can individually place all molecules and determine all the possible ways to identify them. Hence, by placing the N_i^{th} molecule, we define the volume fraction y_i as follows:

The $N_{i+1}{}^{\text{th}}$ molecule can be placed on the quasi lattice:

$$y_i = \frac{sN_i}{N_b + sN} \tag{2.2}$$

$(N_b + sN)(1 - y_i)$ is the number of places in which the first segment of the $N_{i+1}{}^{\text{th}}$ molecule can be placed.

If the first segment is in one of the vacant regions, then $(1 + s(0))(1 - y_i) = 1$. This means

$(1 - y_i) = 1 \Rightarrow y_i = 0$

Each polymer molecule is represented as a chain of s segments. Each was exactly equal in volume to a solvent molecule.

The crucial assumption is that the segment density y_i has a unique value independent of the position.

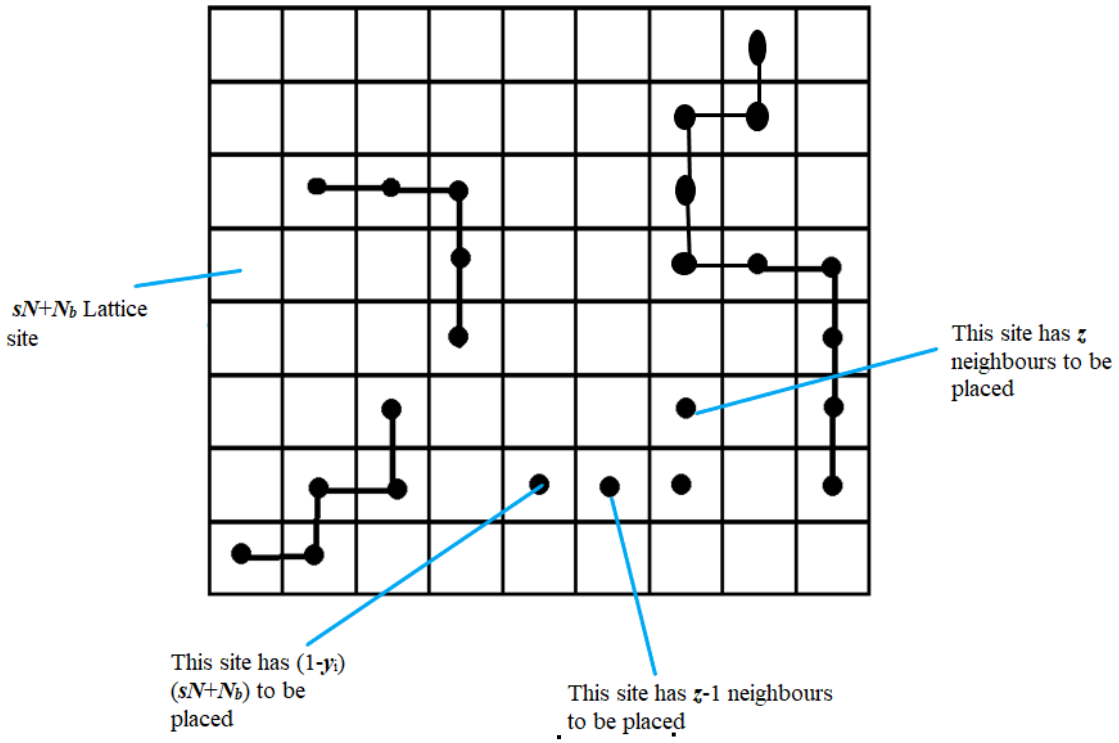


Figure 2-1 The placement of the N_{i+1}^{th} molecule in the lattice

There may be places to place the second segment of the same molecule based on the neighbors for each lattice site when we place the second segment of the same molecule at its second lattice site. It is then possible to place the two segments in a wide variety of ways.

$$(1-y_i)^2 (N_b + sN) z \tag{2.3}$$

There are z–1 neighbors left when we place the third segment of a particular molecule, so we now have a variety of possibilities of how to place the three segments in the same molecule.

$$(1-y_i)^3 (sN + N_b)(z-1)z \tag{2.4}$$

Based on mean field theory, after placing the third segment, the number of neighbors remains z–1. Following the same criteria, the number of ways of placing four segments will be:

$$(1-y_i)^4 \left(N_b + sN\right)(z-1)^2 z \tag{2.5}$$

Ultimately, the number of ways of positioning the $N_{i+1}{}^{\text{th}}$ molecule Ω_{i+1} is:

$$\Omega_{i+1} = \frac{1}{2}(1-y_i)^s \left(N_b + sN\right)(z-1)^{s-2} z \tag{2.6}$$

Due to the segments did not change as a result of replacing them, there is a factor of 1/2 of the result and because the two terminal ends are indistinguishable. The total number of ways w of arranging the entire mixture where the value of i is between 0 and N–1:

$$w = \frac{1}{N!}\prod_{0}^{N-1}\Omega_{i+1} \tag{2.7}$$

In addition, 1/N! takes into account the indistinguishability of the N_2 solute molecules.

By taking the logarithm of the number of ways w, we can calculate the entropy of the solution:

$$\ln w = -\ln(N!) + N\ln\frac{1}{2}\left(N_b + sN\right)(z-1)^{s-2} z + s\sum_{i=0}^{N-1}\ln\left(1-y_i\right) \tag{2.8}$$

Since N is a huge number in the real solution, we can take an integral measurement instead of multiplying by the last term in order to achieve the desired result:

$$\sum_{i=0}^{N\text{-}1}\ln\left(1-y_i\right) = \int_{N_i=0}^{N}\ln\left(1-\frac{sN_i}{sN+N_b}\right)dN_i = -\frac{N_1}{s}\ln\frac{N_b}{sN+N_b} - N \tag{2.9}$$

By using the Stirling substitution for the factorial term $\ln N! = N\ln N - N$, then substitute in ln w:

$$\ln w = -N\ln N + N + N\ln\frac{1}{2}\left(N_b + sN\right)z\left(z-1\right)^{s-2} + s(-\frac{N_1}{s}\ln\frac{N_b}{N_b+sN} - \frac{N}{s}) \tag{2.10}$$

If we choose the case of z =12 (Hexagonal lattice), we can find the entropy of mixing as:

$$\Delta S_{mixing} = k_B \ln w$$

$$\Delta S_{mixing} = \bar{S}_1 - S_1^{\,0} = k_B N \ln\left(\frac{sN + N_b}{sN}\right) + k_B N_b \ln\left(\frac{sN + N_b}{N_b}\right) \tag{2.11}$$

$$= k_B \ln\left[\left(\frac{sN + N_b}{sN}\right)^N \left(\frac{sN + N_b}{N_b}\right)^{N_b}\right]$$

From the above equation, the term $\left(\frac{sN + N_b}{sN}\right)^N \left(\frac{sN + N_b}{N_b}\right)^{N_b}$ is the number of ways of placing the N molecules in the N_l lattice site, which can be simplified by defining volume fraction y and hole fraction h as follows:

$$y = \frac{sN}{sN + N_b} \tag{2.12}$$

$$h = 1 - y = \frac{N_b}{sN + N_b} \tag{2.13}$$

Then, we can express the entropy of mixing as:

$$\Delta S_{\text{mixing}} = k_B \ln\left(y^{-N}(1-y)^{-N_b}\right) \tag{2.14}$$

Therefore, we can calculate the entropy of mixing as:

$$\Delta S_{\text{mixing}} = Rn_2 \ln\frac{n_1 + n_2}{\sigma n_2} + Rn_1 \ln\frac{n_1 + \sigma n_2}{n_1} \tag{2.15}$$

$$\bar{S}_1 - S_1^o = -R\ln\phi_1 - R(1 - \frac{1}{\sigma})\phi_2 \tag{2.16}$$

where ϕ_1 is the volume fraction of solvent:

$$\phi_1 = \frac{n_1}{n_1 + \sigma n_2} \tag{2.17}$$

and ϕ_2 is the volume fraction of solute:

$$\phi_2 = \frac{\sigma n_2}{n_1 + \sigma n_2} \tag{2.18}$$

2.2. Free volume theory and cell models

The Lennard–Jones and Devonshire (LJD) cell model proposes that molecules or segments are preferred points for molecular interactions between neighbors that determine the cell's ability to move, which is determined by a specified pair potential.

According to van der Waals (e.o.s), the equation of state for some imperfect gases is:

$$(P + a\frac{n^2}{V^2})(V - nb) = nRT \tag{2.19}$$

In addition to imperfect gases, Lennard–Jones and Devonshire also developed liquid phase theory to account for the short-range order found in liquids and highly compressed gases. Molecular cells are considered to be enclosed by their nearest neighbors, and molecules can only move within their cells under a certain potential field. It is possible to estimate the cell potential by utilizing a specific close-packed structure and an average spherical symmetry. This is determined by an assumed pair potential to be of the 6-12 form:

$$U(r) = -\frac{A}{r^6} + \frac{B}{r^{12}} \tag{2.20}$$

where r is the distance between two interaction particles, the first part expresses the attraction force, and the second part expresses the repulsive force. The minimum depth of the potential well is expressed by ε^*.

Based on the Prigogine cell model (PCM), which employs two different forms of potentials, such as the harmonic oscillator and square well potential, we van defined the total potential energy U as the sum of the potential energies between molecules i and j, which depends only on the distance between them, as described below:

$$U = \sum_{i<j} \varepsilon\left(r_{ij}\right) \tag{2.21}$$

By using characteristic parameters, we can express the potential energy resulting from intermolecular forces:

$$\varepsilon(r) = \varepsilon^* \varphi\left(\frac{r}{r^*}\right) \tag{2.22}$$

The Lennard–Jones and Devonshire law (6-12 potential) can be expressed as follows:

$$\varphi\left(\frac{r}{r^*}\right) = -2\left(\frac{r^*}{r}\right)^6 + \left(\frac{r^*}{r}\right)^{12} \tag{2.23}$$

The reduced parameters r^* and ε^* represent the coordinates at which the value of $\varepsilon(r_{ij})$ is at the minimum. The intermolecular potential energy is calculated using the Kittel solid-state relation $r^* = \sigma 2^{1/6}$ and can be calculated as:

$$\varepsilon(r) = 4\varepsilon^*\left(-\left(\frac{\sigma}{r}\right)^6 + \left(\frac{\sigma}{r}\right)^{12}\right) \tag{2.24}$$

Multiplying by $r^{*3N}/N!$, then the partition function Q in integral form can be set as:

$$Q = \frac{r^{*3N}}{N!}\int..\int \exp\left\{-\beta\varepsilon^* \sum_{i<j} Q\left(\frac{r_{ij}}{r^*}\right)\right\} d\left(\frac{r_1}{r^{*3}}\right)..d\left(\frac{r_N}{r^{*3}}\right) \tag{2.25}$$

By using characteristic parameters, we can simplify the partition function as follows:

$$Q = r^{*3N} Q^*\left(\frac{kT}{\varepsilon^*}, \frac{V}{r^{*3}}, N\right) \tag{2.26}$$

Then, by using the above expression, we can find the free energy $F = -kT\ln Q$, which can also be expressed as:

$$F = Nf(T,V) \tag{2.27}$$

N, T and P influence the free energy function and partition function:

$$Q = r^{*3N}\left[q\left(\frac{kT}{\varepsilon^*}, \frac{v}{r^{*3}}\right)\right]^N \tag{2.28}$$

We can estimate the characteristic parameters by fitting the equation of state to experimental thermodynamic data as:

$$\tilde{T} = \frac{k_B T}{\varepsilon^*},\ \tilde{v} = \frac{v}{r^{*3}},\ \tilde{p} = \frac{pr^{*3}}{\varepsilon^*} \tag{2.29}$$

When molecules are placed at smaller distances from each other, they apply repulsive forces (Fig. 2.2), which are no longer applied at larger distances. (Statistically, such an occurrence is rare in such circumstances). Consequently, it is reasonable to assume that molecules will be arranged regularly at an average distance. As a result, using the smallest volume per molecule, the irregularities of the density decrease rapidly, resulting in a radical decrease in the number of irregularities within that density.

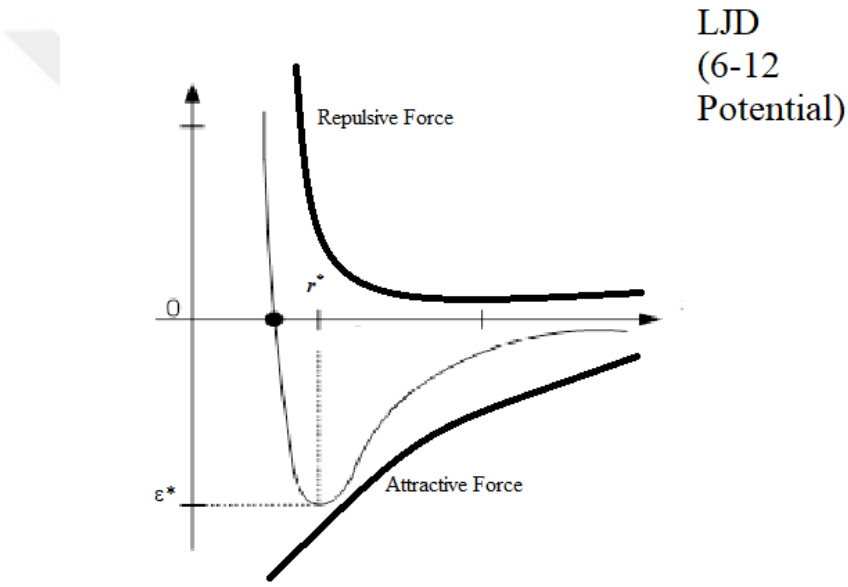


Figure 2-2 Lennard–Jones and Devonshire Potential (6-12)

Based on the cell model, we can explain this very orderly structure as follows:

Molecules can be displaced in the average spherical symmetrical space when the area applied to their cells changes rapidly. A constant displacement of molecules occurs as a result of the increasing volume of particles. For thermodynamic quantities, the displacement effect is negligible as the lifetime of a molecule's cell.

There is a distribution function associated with each particle's energy in the center of the cell. According to our assumptions, the average interaction energy between

neighboring particles only relies on the distance between each molecule, where *r* is determined from the center of the cell. Then, the total energy of a cell becomes equal to the sum of all molecules in its center:

$$E_{tot} = -\frac{1}{2} N\omega(0) \tag{2.30}$$

To calculate the configurational partition function $\Psi(V, T)$ by using the following formula, we can minimize the contribution to the average interaction energy $\omega(r)$ between each neighboring particle that is totally dependent on the central energy of the particle at the center of the cell:

$$\Psi(V,T) = 4\pi \int_{cell} \exp\left[-\beta\left(\omega(r) - \omega(0)\right)\right] r^2 dr \tag{2.31}$$

There are a number of values involved in this function in regard to calculating the center of the cell $\omega(r)$; then, we take the value of $\omega(0)$. In the case of the *N*-particle system $\Psi(V, T)$, the configurational partition function is as follows:

$$\Psi(V,T) = \psi^N \exp\left[-\frac{1}{2}\beta N\omega(0)\right] \tag{2.32}$$

Free energy is then obtained based on the definition of the free energy:

$$F = -k_B T \ln \Psi(V,T) \tag{2.33}$$

Configurational energy and entropy can be obtained from:

$$E_{conf} = k_B T^2 \left(\frac{\partial \ln \Psi}{\partial T}\right)_V = \frac{N\omega(0)}{2} + NkT^2 \left(\frac{\partial \ln \psi}{\partial T}\right)_V \tag{2.34}$$

$$S = k_B \ln \psi + k_B T \left(\frac{\partial \ln \psi}{\partial T}\right)_V = Nk_B \ln \psi + Nk_B T \left(\frac{\partial \ln \psi}{\partial T}\right)_V \tag{2.35}$$

In conclusion, we can express pressure as follows:

$$P = kT \left(\frac{\partial \ln \Psi}{\partial V}\right)_T = -\frac{N}{2}\left(\frac{\partial \omega(0)}{\partial V}\right)_T + NkT \left(\frac{\partial \ln \psi}{\partial V}\right)_T \tag{2.36}$$

All thermodynamic quantities associated with a particle within a cell of adjacent particles are calculated using its configurational partition function. For instance, it is possible to determine the partition function if the molecules are arranged in twelve neighboring face-centered cubic structures. In this case, parameter a is the average distance between the first neighbors, r^* is the distance when ε^* reaches the minimum value, σ is the radius of the molecules, and (a-σ) is the radius of the polyhedron cell structure, as shown in Figure 2-3~~Figure 2-3~~~~Figure 2-3~~.

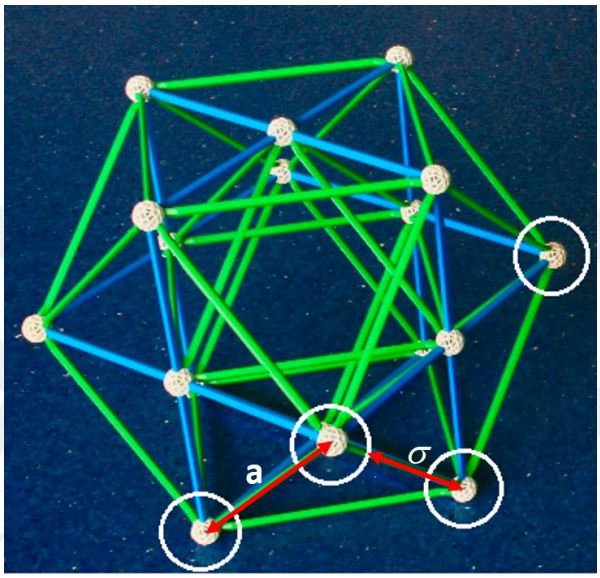


Figure 2-3 Polyhedron cell (twelve neighboring face-centered cubic structures with radius (a-σ))

In this construction of polyhedron n cells, the average potential can be given by the following constraints:

$$\begin{aligned} \omega(0) &= 0, \quad r = 0 \\ \omega(r) &= 0, \quad 0 < r < (a-\sigma) \\ \omega(r) &= \infty, \quad (a-\sigma) < r \end{aligned} \tag{2.37}$$

Then, the partition function becomes $\omega(r) = 0$ when $0 < r < (a-\sigma)$:

$$Q = 4\pi \int_0^{\sigma-a} \exp\left[-\beta(\infty - 0)\right] r^2 dr = 4\pi \int r^2 dr = 4\pi \frac{r^3}{3}\Big|_0^{a-\sigma} = \frac{4\pi}{3}(a-\sigma)^3 \tag{2.38}$$

Now let $a^3 = v/\sqrt{2}$ and $\sigma^3 = v_0/\sqrt{2}$; finally, the partition function is:

$$Q = \frac{4\pi}{3}\sqrt{2}\left(v^{1/3} - v_0^{1/3}\right)^3 \tag{2.39}$$

By applying these results to the equation of state, we have:

$$p = \frac{P}{N} = kT\left(\frac{\partial \ln Q}{\partial V}\right)_T - \frac{1}{2}\left(\frac{\partial \omega(0)}{\partial V}\right)_T = \frac{1}{\beta}\left(\frac{\partial \ln Q}{\partial V}\right)_T \tag{2.40}$$

In comparison to the Lennard–Jones-Devonshire model, which appears to have an average interaction potential structure of the square well potential, the Lennard–Jones-Devonshire model is not appropriate for every quantitative analysis. In the case of liquids of a certain density, it is possible to simplify the process by the structure of the square well potentials.

$$\begin{aligned} \omega(r) - \omega(0) &= 0 \quad \text{for } 0 < r < (a - \sigma) \\ \omega(r) - \omega(0) &= \infty \quad \text{for } (a - \sigma) < r \end{aligned} \tag{2.41}$$

According to these constraints:

$$\omega(0) = z\varepsilon^*\left[C\left(\frac{v^*}{v}\right)^4 - D\left(\frac{v^*}{v}\right)^2\right] \tag{2.42}$$

For the (a-σ) <r strict sphere estimate, we can find the partition function as:

$$Q = 4\pi\int_0^{a-\sigma} \exp\left[-\beta\left(+\infty\right)\right]r^2 dr = \frac{4\pi}{3}\left(r^*\right)^3\left(\frac{v}{v^*}\right)\left[1 - \frac{1}{2^{1/6}}\left(\frac{v^*}{v}\right)^{1/3}\right]^3 \tag{2.43}$$

As this term $4\pi r^{*3}/3$ is a constant, we put it into the equation of state:

$$p = \frac{1}{v}\left[\left(\frac{v^*}{v}\right)^2 z\varepsilon^*\left(2C\left(\frac{v^*}{v}\right)^2 - D\right) + \left(k_B T\left[1 - \frac{1}{2^{1/6}}\left(\frac{v^*}{v}\right)^{1/3}\right]^{-1}\right)\right] \tag{2.44}$$

In some liquid phases consisting of N homogeneous s-mer chains, it is assumed that the molecules are localized under the force that is generated by the neighboring centers of the molecules. The energy applied between the centers of these molecules can be taken into account in a structure such as this. Hence, this state appears when the separation between the neighboring centers as $a \approx d \approx r^*$ is approximately the same for a

uniform mesh formation, where d and r^* are the molecular constants while a depends on temperature and pressure. If the interaction between neighboring cell centers is ignored, $a = r^*$ and the molecules are arranged to form a regular mesh. Due to the destruction of the lattice when it increases with increasing temperature, the result can be ignored, and this destruction can be measured in volume per molecule as:

$$v = \frac{V}{Nr} = \frac{a^3}{\gamma} \tag{2.45}$$

where r is the radius of the polyhedron cell; then, the reduced volume in this destruction is:

$$\tilde{v} = \frac{1}{\left(r^*\right)^3}\frac{V}{Nr} = \left(\frac{a}{r^*}\right)^3 \frac{1}{\gamma} \tag{2.46}$$

By using the combinatorial factor $g(y,N)$, we can find the configurational partition function of this cell model:

$$Q = \psi^N g\left(y, N\right) \exp\left(-\beta E_0\right) \tag{2.47}$$

We can calculate the volume of the first element ψ_1 as the expression given in equation (2.39) by using the configurational partition function outer freedom degrees and using a potential expression similar to that given in equation (2.43).

$$\psi_1 = P_1\left(a - \sigma\right)^3 \tag{2.48}$$

Then, the second element around a spherical surface is $(a\text{-}\sigma)^2$, which depends on the degree of freedom of the destruction:

$$\psi_2 = P_2\left(a - \sigma\right)^2 . \tag{2.49}$$

On a fixed position, we can find the third element as:

$$\psi_3 = P_3\left(a - \sigma\right) \tag{2.50}$$

Obtaining a general result for each chain member as follows:

$$\psi = \prod_{i=1}^{r} \psi_i = \left(\prod_{i=1}^{r} P_i \right) (a - \sigma)^{3c} \tag{2.51}$$

Furthermore, the configurational partition function can be expressed as follows:

$$\psi = \left[\psi(T,V) \right]^{3c} \tag{2.52}$$

$$\Psi = g \left[\psi(T,V) \right]^{3c,N} \exp\left(-\beta E_0 \right) \tag{2.53}$$

Then, the total lattice energy for the s-mer is:

$$E_0 = \frac{1}{2} Nqz\varepsilon^* \left[C \left(\frac{v^*}{v} \right)^4 - D \left(\frac{v^*}{v} \right)^2 \right] \tag{2.54}$$

$$\begin{aligned} 2E_0 &= yN(qz)(\Phi) \\ \Phi &= \varepsilon^* [1.011(v^*/yv)^4 - 2.409(v^*/yv)^2] \\ \omega &= yv / N_s \end{aligned} \tag{2.55}$$

The interaction energy Φ associated with a pair of segments whose potentials are taken to be Lennard-Jones potentials for N molecules as in SS theory, ω is the average energy of neighboring interactions.

The bond vector formed by the s-mer nearest first neighbor molecules is:

$$q_z = s_z - 2s + 2 \tag{2.56}$$

Take a derivative of the partition function using this equation and then use it to obtain the partition function:

$$P = -\left(\frac{\partial F}{\partial V} \right)_T \tag{2.57}$$

Our equation of state has finally been derived:

$$p = \frac{kT}{V} \left[c \left[\left(1 - 2^{-1/6} \left(\frac{v^*}{v} \right)^{1/3} \right)^{-1} + 2\beta qz\varepsilon^* \left(C \left(\frac{v^*}{v} \right)^4 - D \left(\frac{v^*}{v} \right)^2 \right) \right] \right] \tag{2.58}$$

2.3. Vogel–Fulcher–Tammann (VFT) equation and the pressure extended Adam–Gibbs (PEAG) equation

Two different approaches were utilized to analyze the impact of the temperature–pressure relationship on the relaxation time of the system. To be able to describe the relaxation time of the α-process in a complete manner, there need to be four parameters that describe how the relaxation time varies with temperature and pressure.[23]

The relaxation time of a supercooled liquid is generally determined by its temperature; this dependence can be expressed by the Vogel–Fulcher–Tammann (VFT) [24, 25] empirical equation, which is presented below:

$$\tau(T) = \tau_0 \exp(\frac{DT_o}{(T - T_o)}) \tag{2.59}$$

The Adam-Gibbs (AG) theory [25] is based on the main concept of configurational entropy between the thermodynamic and dynamic behavior of glass.

Based on the assumption that different regions cooperatively rearrange each other, the configurational entropy s_c can be derived as:

$$\tau = \tau_0 \exp\left(\frac{c}{Ts_c}\right) \tag{2.60}$$

where s_c is the configurational entropy and c is a material constant.

Because s_c is not in terms of reproducibility, it is related to the excess entropy ($s_{ex} = s_{melt} - s_{crystal}$), and due to its experimental accessibility, the proportionality between s_{ex} and $s_{crystal}$ refers to the relationship between s_{ex} and $s_{crystal}$ as the proportionality constant, so the value of c is only affected by the proportionality constant. Accordingly, the $s_{crystal}$ can be stated as follows:

$$s_{crystal}(T) = \frac{\Delta H_{melt}}{T_{melt}} - \int_{T}^{T_{melt}} \frac{\Delta C_p(T')}{T'} dT' \tag{2.61}$$

where $\Delta c_p = c_p^{\,melt} - c_p^{\,glass}$ is the excess heat capacity.

There are many polymers that do not melt, and various methods must be used to calculate $s_{crystal}$ because there is no melt observed in those polymers.

The VFT expression for the temperature dependence of the relaxation time $\Delta c_p (\Delta c_p = \frac{K}{T})$ can be derived by integrating the equation above with $T_o = T_k$, where T_k is the Kauzmann temperature where excess entropy disappears and an equilibrium value is obtained.

These two theories are used to explain the phenomenon of liquids that do not crystallize when they are cooled at sufficiently high rates. The process of supercooling occurs in these theories, which eventually leads to entering the state of glassiness, where molecular motions of the system are frozen in time according to the time scale of the experiment, and finally entering the state of supercooling. It has been found that a liquid that has been supercooled for a long enough period of time can also reach a glassy state by applying high pressure to it after it has been supercooled for a long enough period of time. This allows the liquid to achieve a state that is indistinguishable from glass through the application of high pressure. In the presence of pressure and temperature changes, both of which result in a slowing of molecular motion, molecular motion is slowed down as well. We can separate thermal and volumetric effects that contribute to the glass transition by using these two different approaches, allowing us to gain a better understanding of the process of the glass transition.

2.4. Lattice Cluster Theory

Any polymer system's thermodynamic properties are greatly influenced by the interactions and chemical constructions that occur within it. However, there has been little effort in developing a molecular theory for polymer melts that is capable of accurately predicting how chemical structure and specific interactions will affect the thermodynamic properties of the melts. In this field of polymer melts and mergers, lattice cluster theory (LCT) is a tremendous tool for understanding how a variety of molecular factors, such as the structure of monomers, affect the thermodynamic properties. The applications of LCT use the simplest polymer model whereby all the united atoms of the monomers of the

same species interact with the van der Waals energy averaged over the monomers of all species. It is therefore possible to describe a compressible polymer melt in terms of a single van der Waals energy when discussing a polymer melt. For the new model, a systematic expression is provided by the Helmholtz free energy for the LCT based on the new data. Calculations are presented that illustrate how a specific interaction can influence the thermodynamic properties of a polymer melt in order to demonstrate how these properties can be meticulously determined by specific interactions.

2.5. Simha-Somcynsky (SS) lattice hole theory

The arithmetical thermodynamics of polymers can be derived from statics, and molecules can be arranged in lattice sites in all spaces that can divide them into sectors. Employing two different forms of potentials (harmonic oscillator and square well potential) and according to the Lennard–Jones-Devonshire (LJD) and Prigogine cell models intended for analysis of *s*-mer systems, we can assume that the polymer molecule glides within a potential well (or cell) created by molecules at neighboring ends.

Simha-Somcynsky's equation of state (e.o.s.) has been based on the lattice-hole model, which is capable of providing temperature- and pressure-dependent fractions of occupied sites. The Simha-Somcynsky equation of state (SS EOS) is a well-known equation for predicting the fractions of occupied sites and complementary holes in polymers, as well as the *P*, *V*, and *T* behavior of polymers, so that polymers with holes have an increased degree of irregularity (entropy). The potential energy between any two segments of the molecule for a close-packed hexagonal cell geometry z =12 and with nonadjacent neighbor contribution and by using the Kittel solid state:

$$\varepsilon(r) = \varepsilon^* \left[A\left(\frac{r^*}{r}\right)^{12} - 2B\left(\frac{r^*}{r}\right)^{6} \right] \tag{2.62}$$

In the case of combinations of N molecules with *s*-mer segments, the configurational partition function can be expressed as follows:

$$Z_{conf} = Z(V,T) = f(T,V)^{3cN}\, g(N,y) \exp\left(-\beta E_0\right) \tag{2.63}$$

The combinatorial factor g can be expressed in terms of N and y, and it characterizes the number of distinguishable ways of placing N molecules at N_l lattice sites. $f(T,V)^{3cN}$ is the cell partition function that has an external degree of freedom of $3c$. E_0 is the total energy when each segment is placed on its site:

$$E_0 = \frac{1}{2} q_z N \varepsilon^* \left[A \left(\frac{\upsilon^*}{\upsilon} \right)^4 - 2B \left(\frac{\upsilon^*}{\upsilon} \right)^2 \right] \tag{2.64}$$

Each molecule with s-segment forms of the first neighbor intermolecular pairs, which is expressed by q_z:

$$q_z = s(z-2) + 2 \tag{2.65}$$

where the coordination number z is the number of nearest neighbors. The total degrees of freedom $3c$ for the elastic ideal chain in an s-mer molecule can be written as:

$$3c = 3s - (s-1) - (s-2) = s + 3 \tag{2.66}$$

For the independent s segments, the total number of degrees of freedom will be $3s$, but if we put a stretching constraint on the s-mer, then the contribution of $s-1$ should be reduced from the total contribution. Similarly, the angular constraint between the three segments reduces another $s-2$ contribution from the total one. The total number of degrees of freedom for an elastic ideal chain corresponds to $3c = s + 3$, which is commonly used for long polymer chains.

Based on the equation of state of the free energy, we can derive the following:

$$\frac{\tilde{P}\tilde{V}}{\tilde{T}} = \frac{\tilde{V}^{1/3}}{\tilde{V}^{1/3} - 2^{-1/6}} + \frac{2}{\tilde{T}} \left[\frac{A}{\tilde{V}^4} - \frac{B}{\tilde{V}^2} \right] \tag{2.67}$$

In the following formulae, the bond between theoretical and experimental quantities is explicitly expressed by reducing the parameters as follows:

$$\tilde{P} = \frac{P}{P^*}, \qquad \tilde{V} = \frac{V}{V^*}, \qquad \tilde{T} = \frac{T}{T^*} \tag{2.68}$$

In this case, the reducing parameters are shown as follows:

$$P^* = \frac{q_z \varepsilon^*}{\upsilon^*}, \qquad V^* = \frac{m_\circ \upsilon^*}{N_A}, \qquad T^* = \frac{q_z \varepsilon^*}{ck} \tag{2.69}$$

where the segmental molecular mass is expressed by m_o. Using these three parameters, one will obtain a parametric expression

$$(\frac{P^*V^*}{T^*})m_o = (\frac{c}{s})R \tag{2.70}$$

which also involves another structural parameter c known as degrees of freedom.

Then, the configurational partition function Z_{conf} is expressed as:

$$Z_{conf} = \left[\upsilon_f\left(\tilde{V},y\right)\right]^{cN} g\left(N,y\right)\exp\left[-\frac{E_0\left(\tilde{V},\tilde{T},y\right)}{kT}\right] \tag{2.71}$$

Here, the combinational factor $g(N, y)$ can be expressed by

$$g\left(N,y\right) = y^{-N}\left(1-y\right)^{-sN(\frac{1-y}{y})} \tag{2.72}$$

The total energy E_0 when each segment is placed on its site for each s-mer is:

$$E_0 = \frac{1}{2}yNq_z\varepsilon^*\left[A\left(\frac{\upsilon^*}{\omega}\right)^4 - 2B\left(\frac{\upsilon^*}{\omega}\right)^2\right] \tag{2.73}$$

The average energy of neighboring interactions is $\omega = yV/Ns$, and the number of lattice holes expressed by the free volume υ_f is:

$$\upsilon_f = \upsilon^*\left\{y\left[\left(y\tilde{V}\right)^{1/3} - 2^{-1/6}\right] + \left(1-y\right)\left(y\tilde{V}\right)^{1/3}\right\}^3 \tag{2.74}$$

Furthermore, by combining all these pieces of information, we are able to find a certain formula of this configurational partition function that we can use to solve this problem:

$$\begin{aligned} F_{conf} &= -kT\ln Z_{conf} \\ &= NkT\ln y + kTsN\left(\frac{1-y}{y}\right)\ln\left(1-y\right) \\ &\quad -3kTcN\left\{\ln\left[\left(y\tilde{V}\right)^{1/3} - 2^{-1/6}y\right] + \frac{1}{3}\ln\left(v^*\right)\right\} \\ &\quad +\frac{1}{2}yNq_z\varepsilon^*\left(y\tilde{V}\right)^{-2}\left[1.011\left(y\tilde{V}\right)^{-2} - 2.409\right] \end{aligned} \tag{2.75}$$

Then, we can obtain the equilibrium condition for this free energy:

$$\left(\frac{\partial F}{\partial y}\right)_{\tilde{V},\tilde{T},c/s}=0$$
$$\frac{s}{3c}\left[\frac{s-1}{s}+\frac{\ln(1-y)}{y}\right]-\frac{\eta-\frac{1}{3}}{1-\eta}-\frac{y}{6\tilde{T}}\left(y\tilde{V}\right)^{-2}\left[2.409-3.033\left(y\tilde{V}\right)^{-2}\right]=0 \quad (2.76)$$

The Eyring shear viscosity η depends on the $y,\tilde{V}$ terms as follows:

$$\eta=2^{-1/6}y(y\tilde{V})^{-1/3}.$$

Additionally, we can find the pressure as the derivative of free energy by volume at a certain temperature as follows:

$$P=-\left(\frac{\partial F}{\partial V}\right)_T=P\left[\tilde{V},\tilde{T};y\left(\tilde{V},\tilde{T}\right)\right] \quad (2.77)$$

As a result, we can obtain the equation of state (e.o.s) as:

$$\frac{\tilde{P}\tilde{V}}{\tilde{T}}=\frac{1}{1-\eta}+\frac{2y}{\tilde{T}}\left(y\tilde{V}\right)^{-2}\left[1.011\left(y\tilde{V}\right)^{-2}-1.2045\right] \quad (2.78)$$

2.6. Relaxation Time Theory

By using the Stokes–Einstein–Debye (SED) expression [7], orientational molecular diffusivity can be shown to be a quantitative indicator of viscosity. Einstein's equations for explaining diffusion are derived from the theory of hydrodynamics. However, it is also possible to explain the relationship between the relaxation time τ and the viscosity η by using the following equations:

$$\tau=\frac{4\pi\eta r^3}{3k_BT} \quad (2.79)$$

where k_B is the Boltzmann constant and r is the radius for each molecule.

It is possible to interpret the nonequilibrium properties of materials by extending the thermodynamic properties of materials, such as viscoelasticity and physical aging.

Various equilibrium and kinetic processes have also been expressed using the hole fraction to describe phenomena such as viscosity, ionic conductivity, and other relevant aspects of materials.

It is possible to express Eyring's shear viscosity as a function of jumping frequency k' [16, 17, 26] as:

$$\eta = \frac{6s}{q_z h} \frac{k_B T}{\sqrt{2}\upsilon k'} \tag{2.80}$$

where $q_z h/s$ is the number of available nearest neighboring holes and υ is the molar volume of a segment. The Eyring jumping frequency of a molecule to a hole with activation energy E_a can be expressed as [16-19, 26]:

$$k' = \kappa \frac{k_B T}{h_p} \frac{Z^*}{Z} \exp \frac{-E_a}{k_B T} \tag{2.81}$$

This is the Eyring frequency fraction kT/h_p, h_p is Plank's constant, the respective partition functions of Z in the initial state and Z^* in the activated state and κ is the transmission coefficient. Z^*/Z defines the ratio of the concentrations of the respective states. We assume that the vibrational modes of the initial state change into a translational mode when segments are transported (activated state).

The activation energy is linearly related to the sublimation energy E_s in equilibrium that can give by $(1-h)qz\Phi/2$, and inversely related to the hole fraction as a measure of the number of neighboring holes. Hence, the activation energy can be expressed as follows [16, 17, 26, 27]:

$$E_a = \frac{1}{2} \frac{1-h}{h} a' q_z \Phi \tag{2.82}$$

where according to the SS theory, a' is the proportionality constant, and Φ is the interaction energy associated with a pair of segments whose potentials are taken to be Lennard–Jones potentials.

According to this equation, the scaled relaxation equation can be written as follows:

$$\ln(\tilde{\tau}\tilde{T}) = \alpha Y_h, \qquad Y_h = \frac{1-h}{h}\frac{1}{\tilde{T}} \tag{2.83}$$

$$\tau^* = \frac{8\pi r^3 s h_p}{\sqrt{2} q_z h\nu\kappa k T^*} \qquad \text{and} \qquad \alpha = a' \frac{q_z \Phi}{2kT^*} \tag{2.84}$$

where the scaled relaxation time is $\tilde{\tau} = \tau / \tau^*$ and α is the slope of the relaxation equation. Here, Y_h is called the thermo-occupancy function. This model can satisfy the logarithm of relaxation time data in terms of the thermo-occupancy function for a wide range of temperatures and pressures for polymer species.

Here, $h\nu$ and Φ are sluggishly varying functions of temperature and pressure [16, 17, 26-28]. To keep them in the coefficients, they are included. The quantity Y_h is the ratio of occupied-to-unoccupied sites (holes) divided by the scaled temperature. There are two ways in which Y_h donates to the calculation of relaxation in this situation either by using the structural occupancy or by correlating inversely with temperature as well as interrelated with the vibrational energy of the relaxing molecule. Additionally, we can refer to Y_h as the "thermo-occupancy function" that correlates relaxation to the occupancy function.

According to the equation below, the derivative of the logarithmic relaxation time with respect to h at constant temperature produces the following expression:

$$\left.\frac{\partial \ln \tilde{\tau}}{\partial h}\right|_{\tilde{T}} = -\frac{\alpha}{h^2}\frac{1}{\tilde{T}} \tag{2.85}$$

The derivative of the logarithm of relaxation with respect to the hole fraction, named relaxiholibility (derived from relaxation and hole fraction), has a negative coefficient such that an increase in hole fraction has an effect of a reduction on the relaxation time. The relaxation time is almost inversely related to the increase in hole fraction.

3. APPLICATION OF SS THEORY

By analyzing the hole fraction of the site, the SS theory has been able to express the irregularity of the site. A polymer's thermodynamic characteristics are also expressed in such a way that the thermodynamic quantities of the polymer can also be expressed in terms of the hole fraction of the polymer. Therefore, determining the hole fraction is one of the most significant steps in the procedure and is based on the degree of freedom of the polymer. In our investigations of the PVAC polymer, we combined the theory-specific reduced scaling parameters for scaling pressure, scaling temperature and scaling volume. These parameters are simultaneously fitted to the density data with average and maximum relative percentage error in volume given by meters of our investigations.

The parameters of the system, which have the characteristic features, are obtained by overlapping the experimental surface and the theoretical surface. *N* systems of equations are obtained by overlapping the surfaces of the experimental and theoretical $\tilde{P}\tilde{V}\tilde{T}$. The system of equations will be solved by the Newton Raphson method [15]. However, the number of unknowns is less than the number of data points, so the pseudo inverse matrix technique must be used to obtain some optimized solutions. We employed the Mathematica package program to solve this set of equations using the pseudoinverse function in Mathematica. To obtain the phenomenological degrees of freedom of the system, we float its values and then choose one with the least error in the percentage error in the volume that is calculated as per the average of the relative deviation between the experimental and theoretical volume data as follows:

$$\%\Delta V = \frac{100}{N}\sum \frac{V_{theory} - V_{\exp}}{V_{\exp}} \tag{3.1}$$

where V_{exp} is the specific volume as per the book of Zoller and Walsh called "Standard Pressure–Volume-Temperature Data for Polymers", V_{theory} is the specific volume calculated from the SS theory using the data above reference and *N* is the amount of data.

The maximum error is found with average errors in the percentage of all pressure and temperature values.

Thus, we apply the above scheme to the PVAc polymer to obtain the optimal V^* , T^*, and P^* parameters as 0.8269×10^{-3} m^3/kg, 9989.3 K and 975.4 MPa, respectively, were found for the total degrees of freedom $3c = 2712$ with the number of segments $s = 2709$. The mean error and maximum error in volume are calculated as 0.072% and 0.27%, respectively. All these parameters are tabulated in Table 3.1~~Table 3.1~~~~Table 3.1~~.

For PVAc, we fitted the hole fraction data obtained from SS theory to the scaling relationship for the behavior of polymers over a wide range of pressures and temperatures to obtain a comprehensive understanding of the $h(P,T)$ relationship.

$$h = \frac{1}{h_0 + h_1\tilde{P}} + \frac{\tilde{T}}{h_2 + h_3\tilde{P}} \tag{3.2}$$

where $h_0 = -8.707 \pm 0.023$, $h_1 = -17.39 \pm 0.26$, $h_2 = 0.1678 \pm 0.0002$ and $h_3 = 0.4216 \pm 0.\ 0024$. Using these parameters, we may predict the hole fraction computed from the SS theory. The predicted hole fraction deviates from the obtained hole fraction with a mean deviation of 0.024% and maximum deviation of 0.15%. This is pretty well in the limit of the computed values. Eq. (3.2) can be used for any purpose in other applications, such as calculating relaxation, which we discuss in the next section.

Table 3.1 Computed characteristic parameters for SS-EOS.

Parameters	PVAc
s	2709
$3c$	2712
$V^*(\mathrm{m}^3/\mathrm{kg})$	0.8269×10^{-3}
$T^*(\mathrm{K})$	9989.3
$P^*(\mathrm{MPa})$	975.4
$m_0(\mathrm{kg})$	34.35
$\langle\varepsilon^*(\mathrm{K})\rangle$	333.3
$<h\tilde{V}>$	0.09648
$-<\Phi(K)>$	0.889±0.1
$\langle\upsilon^*(m^3/mol)\rangle$	28.41×10^{-6}
$\%\Delta V$	0.072
$\%\Delta V_{\max}$	0.27

3.1. The Parameters associated with the relaxation model

By the non-Newtonian viscosity model, we can find the scaling parameters of the SS theory and compare them with the SS theory result. This relation can potentially delineate an appropriate implementation for fitting pressure- and temperature-dependent viscosity data. The characteristic thermodynamic parameters P^*, V^*, T^* and the hole fraction are obtained by fitting the *PVT* data to the Simha-Somcynsky equation of state.

According to Table 3.2~~Table 3.2~~~~Table 3.2~~ for PVAc, the root mean square (RMS) of relaxation time is calculated by:

$$\%\mathrm{RMS} = \frac{100}{N}\sqrt{\sum\left(\tau_{fit} - \tau_{\exp}\right)^2} \tag{3.3}$$

where τ_{fit} is the relaxation time measured from the scaled relaxation equation and is the experimental value τ_{exp}, CC is the correlation coefficient and $\%\Delta f$ is the average percentage deviation from linearity of the scaled relaxation equation as given by:

$$\%\Delta f = \frac{100}{N}\sum\frac{f_{fit} - f_{\exp}}{f_{\exp}} \tag{3.4}$$

The *P*, *V*, and *T* data from theoretical and experimental data, along with Eq. (2.78), can be used to determine the reduced pressure *P**, reduced volume *V**, reduced temperature *T** and degree of freedom *c*/*s* by a variety of methods. To determine the best *c*/*s* parameter that matched well with the experimental data, the pseudo inverse matrix technique (PIMT) and Newton Raphson method (NRM) were used in conjunction with the Mathematica program to apply the pseudo inversion matrix technique (PIMT). The following tables provide a comparison of the characteristic parameters originating from the NRM and PIMT methods for PVAc.

The parameters presented in the table above are fit with the average percentage error in specific volume 0.0724% and the average interaction energy per segment where the K (Kelvin) unit is used for the energy scale. The volumetric interaction parameter for PVAc with 34.3595 cc/mol is slightly high. Approximately 0.27% was found to be the maximum percentage error between the experimental and theoretical data.

Table 3.2 Fitting parameters values with respect to the equation **(2.83)~~(2.83)~~~~(2.83)~~ (3.3)~~(3.3)~~~~(3.3)~~** and **(3.4)**.

PVAc	$10^6\tau$*(s)	α	a'	$10^6\kappa$	%RMS	$\%\Delta f$	CC
	0.14	0.031	0.04	0.0924	1.13	0.04	0.9763

3.1.1. Volume Temperature Relation

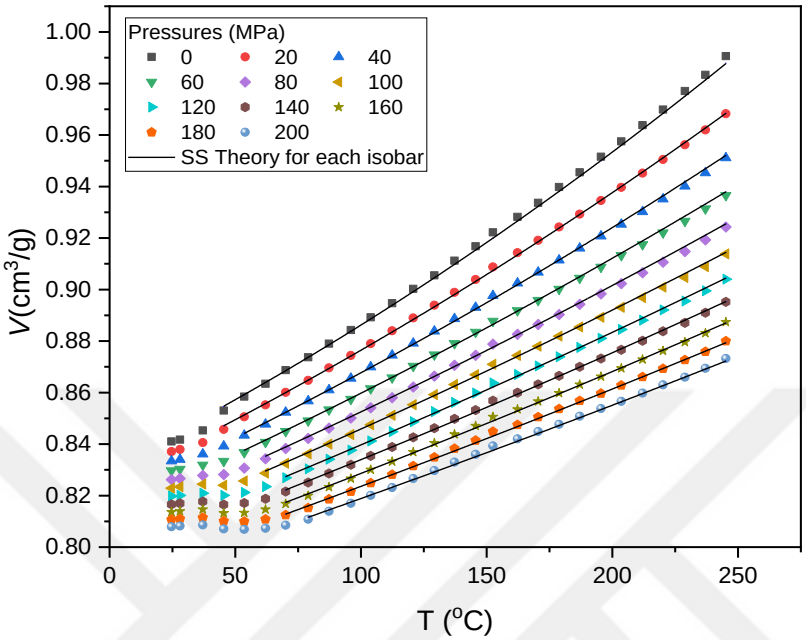


Figure 3-1 Specific volume versus temperature for pressures from ambient to 200 MPa.

In Figure 3-1, the specific volume is plotted versus temperature. The experimental data taken from Zoller and Walsh[29] are represented with different symbols for each pressure. The line through the data are obtained from the SS theory for PVAc. As seen from Figure 3-1, we can observe that the experimental errors increase at low pressure with high temperature precincts. In Figure 3-1, the nonfitted part is glassy state data. A mechanism whereby the molecular motions of the system are frozen in the time scale of the experiment, which does not imply that.

According to Section 2.3~~2.3~~~~2.3~~ To better understand the glass transition process, we can separate thermal effects from volumetric effects by using two different approaches to the glass transition [30].

3.1.2. Volume with respect to Pressure

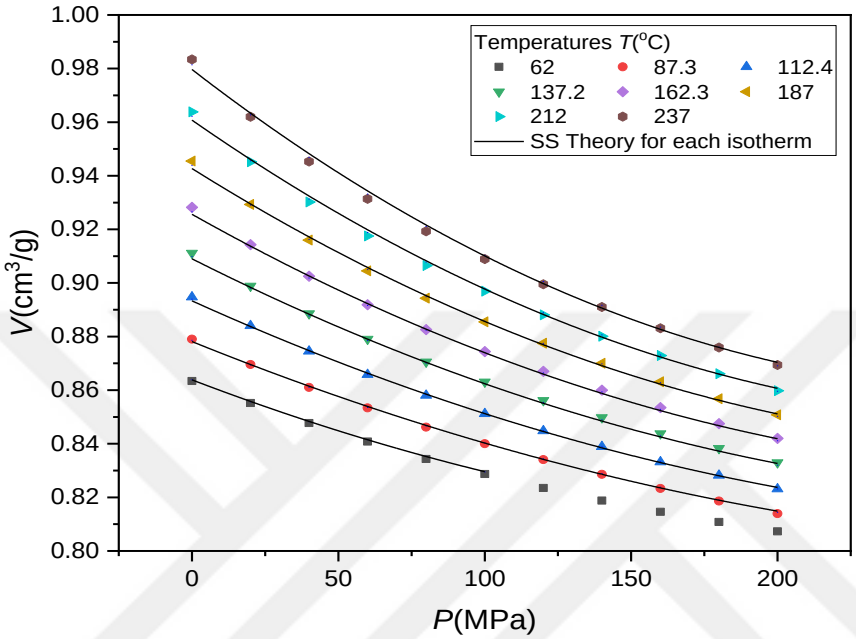


Figure 3-2 Specific volume versus pressure at different temperatures

In Figure 3-2. The shape points illustrate experimental data, and the fitting lines illustrate the SS theory for PVAc.

In Figure 3-2, the specific volume is plotted versus pressure. The experimental data taken from Zoller and Walsh [29] are represented with different symbols for each temperature. The line through the data are obtained from the SS theory for PVAc. As seen from Figure 3-2, we can perceive that the experimental error increases at low pressure in the high temperature zones. The linear fit for each isothermal dependency of structural relaxation in SS theory decreases rapidly with increasing pressure up to 200 MPa. Based on the figure, the nonfitted part of the system is located up to 100 MPa and under an approximate value of the specific volume of 0.85 cm3/g as a consequence of the glassy case region approaches outlined in Section 2.3~~2.3~~2.3~~.3~~.

3.1.3. Hole fraction with respect to pressure for some temperatures

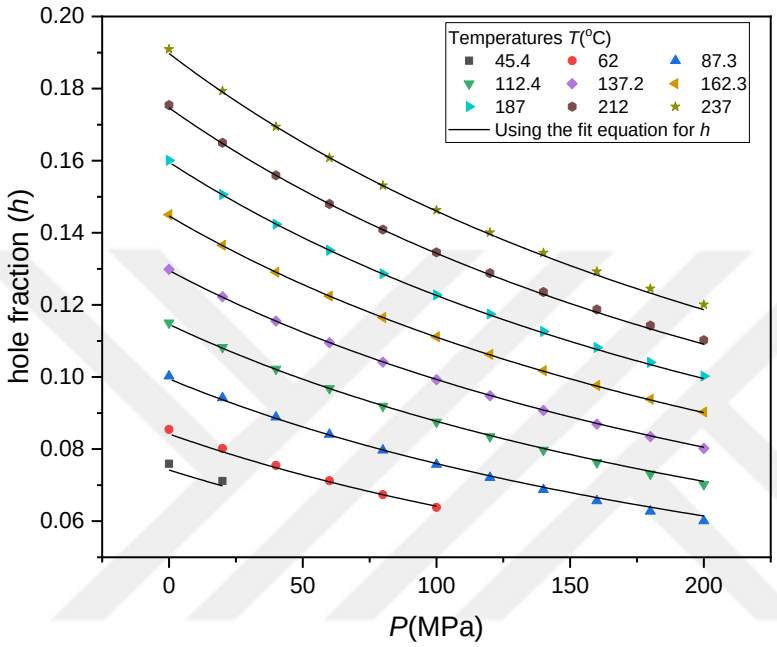


Figure 3-3 Change in hole fraction with pressure at different temperatures

In Figure 3-3. To illustrate how the hole fraction changes with pressure, the shape points illustrate experimental data, and the fitting lines illustrate the SS theory for PVAc.

The general consensus is that compression occurs when pressure is applied to polymer structures. Due to this, the hole in the lattice has been caused as a result of reduction will be made to the structure.

It is common for the hole fraction to decrease with increasing temperature. In high-pressure zones. As a function of pressure, the reduction in hole fraction is regular, and the variation curve is close to linearity.

3.1.4. The Logarithm of Relaxation Time in Terms of Thermo-Occupancy Function Relations.

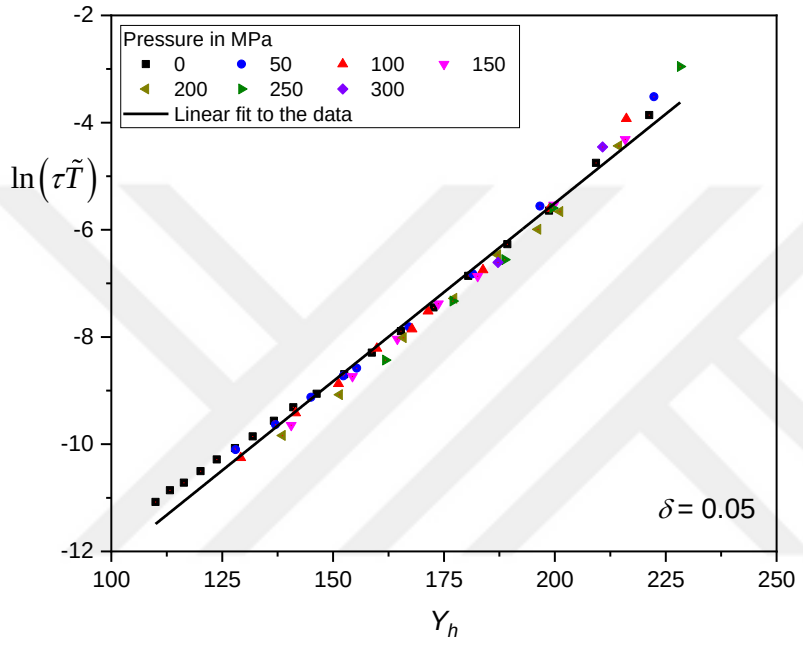


Figure 3-4 The logarithm of relaxation time data ($\ln \tilde{\tau}\tilde{T}$) in terms of the thermos-occupancy function for a wide range of pressures for the PVAc polymer with the best fit lines

In Figure 3-4. At the additive hole fraction necessary for relaxation ($\delta = 0.05$) with a mean percentage %RMS of 1.13%, the deviation from linearity (%Δf) is 0.041. The slope of the curves that show the slope of the relaxation equation is given by the parameter α of approximately 0.031, as shown in Table 3.2~~Table 3.2~~~~Table 3.2~~ values of the fitting parameters in equation (2.83) and some fitting errors. There is a low activation energy coefficient a' of 0.04, owing to the decrease in the parameter, which is why the activation energy coefficient discussed above was so low, as the total interaction energy increases with increasing chain length, which is responsible for the activation energy coefficient.

Thus, the end effect has an important contribution to relaxing the molecule and causes an increase in relaxation time.

Table 3.2~~Table 3.2~~~~Table 3.2~~ provides the total energy and activation energy coefficients of the molecule, and in equation (2.83), some fitting errors are present, and the coefficient a' of 0.04 has a low activation energy coefficient. It can be concluded that these parameters have an incredibly significant involvement in the relaxation of the melt polymer, resulting in an increase in relaxation time.

Table 3.2~~Table 3.2~~~~Table 3.2~~ also provides the transportation coefficient k, the values of the fitting parameters in equation (2.83), and we observed that the fitting errors increased with increasing chain length. A given scaling relaxation time parameter τ^*, which is measured with a unit per second per Kelvin, has a corresponding value when the temperature is high enough and the hole fraction is large enough; the parameter τ^* decreases in value as the chain length increases.

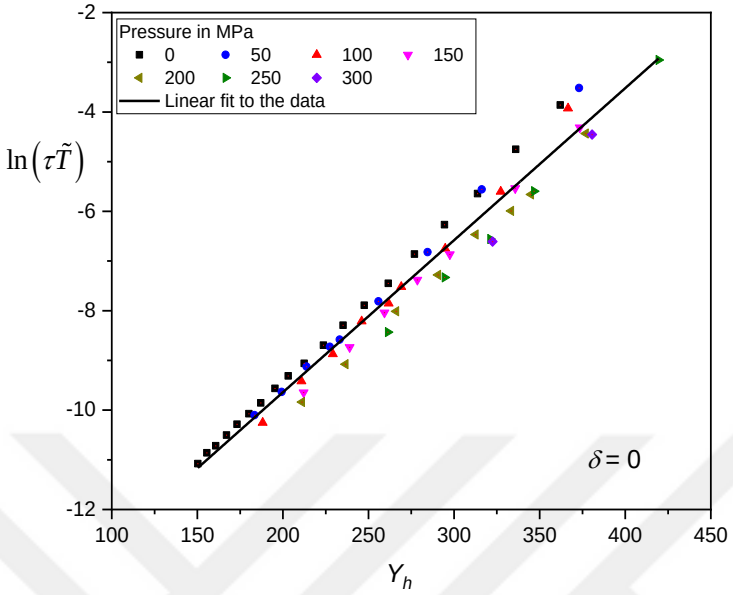


Figure 3-5 The logarithm of relaxation time data ($\ln \tilde{\tau}\tilde{T}$) in terms of the thermos-occupancy function for a broad range of pressures for the PVAc polymer with no additive hole fraction included ($\delta = 0$)

The small decrease in the additive hole fraction from 0.05 to 0 increases Y_h and then has an effect of decreasing the relaxation time. An increase in thermo-occupancy almost linearly correlates with this relaxation time.

In this Figure 3-5. Show the relation between the logarithm of relaxation time data in term of thermos-occupancy function for a wide range of pressure (0-300) MPa.

For PVAc with the best fitting line with no additive hole fraction included that required for linearize the relation. The solid line is the best fit line through the data with a slope of 0.031.

We can perceive that an increase in thermo-occupancy almost linearly correlates with this relaxation time.

The data shows curvature increasing the pressure at each temperature especially apparent at high thermos-occupancy region.

3.1.5. Scaling Relaxiholibility Versus Hole Fraction Relation

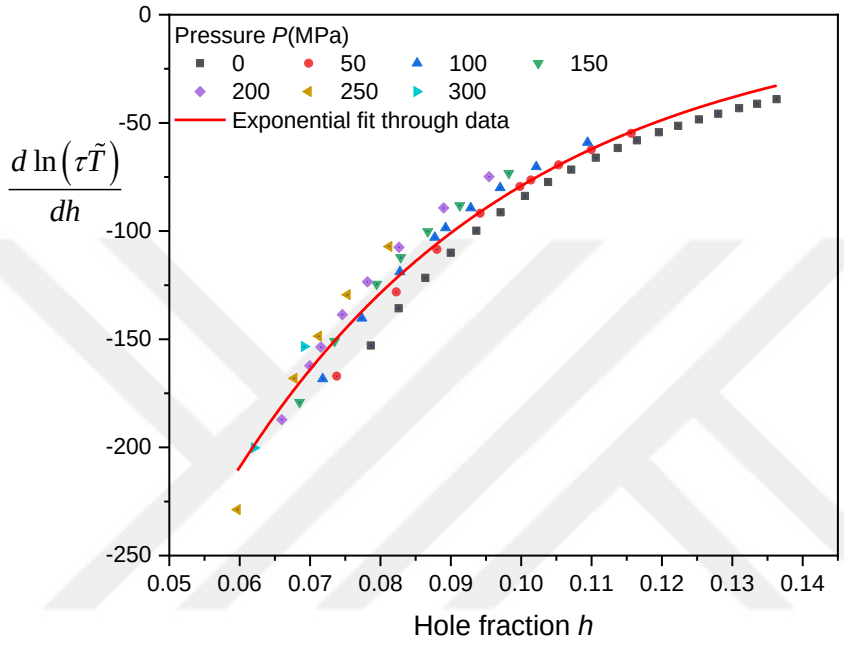


Figure 3-6 A comparison of relaxiholibility versus hole fraction at different pressure

In Figure 3-6. Essentially, the solid curve is the result of exponentially fitting all of the data. In the presence of a low hole fraction, the relaxation time increases exponentially and reaches saturation at the same time. The low hole fraction has a strong influence on the relaxation time; even small changes in the hole fraction can cause a substantial response in relaxation time. When the hole fraction in the molecular transport system is relatively small, the free volume is very sensitive to how mobile the molecular transport system is. There is a tendency, however, to have a linear relationship between the logarithm of relaxation time and the hole fraction as the hole fraction increases. This means that as long as the hole fraction increases, the change in relaxation time saturates to a constant value, when the hole fraction reaches to the highest values, this can be due

the fact that the large hole fraction is sufficient to relax a molecule independent of their structural pattern either bulky or slimy. A formula for determining the relaxiholibility based on the parameters of the structure.

However, the relaxation time leads to sharp decreases at low hole fractions.

$$\left.\frac{\partial \ln \tilde{\tau}}{\partial h}\right|_{\tilde{T}} = -\frac{\alpha}{h^2}\frac{1}{\tilde{T}} \tag{3.5}$$

In accordance with this equation $y = ae^{bx}$, the relaxiholibility increases exponentially with any increase in the hole fraction and saturates to a constant value 13.50×10^3. Applying this formula by dividing the relaxiholibility by the parameters of the molecule's structure, $a = -898.096 \pm 52.11588$ and $b = -24.289 \pm 0.723$. An increase in the hole fraction results in a decrease in the relaxation time, which indicates a negative coefficient.

CONCLUSION

A theoretical model is presented in this paper that incorporates both the Eyring Significant Structure (ESS) and the statistical thermodynamics of liquids SS theory. The results of the application of this theoretical model show that the hole fraction of the model plays a significant role in the effect of temperature and pressure on the hole fraction and is a significant indicator of the quantity of free volume. It is possible to use this model for PVAc to satisfy the logarithm of relaxation time data for a wide range of temperatures and pressures. In light of the logarithms of relaxation and hole fractions, we can determine the new thermodynamic quantity called relaxiholibility. It is the combination of relaxation and hole fraction that is responsible for the new thermodynamic quantity. Because the dynamic quantity has a negative coefficient, an increase in the hole fraction will result in a decrease in relaxation time as a result. There was a rapidly increasing relaxiholibility with increasing hole fraction for the polymers studied, and saturation occurred at an approximately 0.135-hole fraction. When we consider the saturated value of hole fractions, the relaxation time is expected to sharply decrease with the increase in hole fraction as the saturation value of the hole fractions approaches the maximum value. As a result, there is almost a direct correlation between relaxation time and hole fraction when considering the saturated value. This model will be an important asset in the work of relaxation time in dielectric studies of materials. As materials studies are some designs of the materials necessitated by the synthesis of polymers for the purpose of dielectric materials, the relaxation time relationship will be important in these studies.

REFERENCES

[1] Yahsi, U., Coskun, B., Yumak, A., Boubaker, K., Tav, C. (2015) Relaxation time of polypropylene glycol and polypropylene glycol dimethylether-like polymers in terms of fluid-phase temperature and pressure dependent hole fraction European Polymer Journal, 68, 226-232.

[2] Paluch, M., Roland, C.M. (2003) The Avramov model of structural relaxation Journal of Non-Crystalline Solids, 316(2-3), 413-417.

[3] Paluch, M., Pawlus, S., Roland, C.M. (2002) Pressure and temperature dependence of the alpha-relaxation in poly(methyltolylsiloxane) Macromolecules, 35(19), 7338-7342.

[4] Paluch, M., Hensel-Bielowka, S., Psurek, T. (2000) Analysis of "equation of state" for supercooled liquid Journal of Chemical Physics, 113(10), 4374-4378.

[5] Kriegs, H., Gapinski, J., Meier, G., Paluch, M., Pawlus, S., Patkowski, A. (2006) Pressure effects on the alpha and alpha ' relaxations in polymethylphenylsiloxane Journal of Chemical Physics, 124(10).

[6] Mierzwa, M., Floudas, G., Dorgan, J., Knauss, D., Wegner, J. (2002) Local and global dynamics of polylactides. A dielectric spectroscopy study Journal of Non-Crystalline Solids, 307, 296-303.

[7] Stickel, F., Fischer, E.W., Richert, R. (1996) Journal of Chemical Physics, 104, 2043-2055.

[8] Hansen, C., Stickel, F., Richert, R., Fischer, E.W. (1998) Journal of Chemical Physics, 108, 6408-6415.

[9] Pakula, T. (2000) Journal of Molecular Liquids, 86, 109-121.

[10] Dlubek, G., Shaikh, M.Q., Krause-Rehberg, R., Paluch, M. (2007) Effect of free volume and temperature on the structural relaxation in polymethylphenylsiloxane: A positron lifetime and pressure-volume-temperature study Journal of Chemical Physics, 126(2).

[11] Cohen, M.H., Turnbull, D. (1959) Journal of Chemical Physics, 31, 1164-1169.

[12] Turnbull, D., Cohen, M.H. (1970) Journal of Chemical Physics, 52, 3038-3041.

[13] Psurek, T., Ziolo, J., Paluch, M. (2004) Analysis of decoupling of DC conductivity and structural relaxation time in epoxies with different molecular topology Physica a-Statistical Mechanics and Its Applications, 331(3-4), 353-364.

[14] Pasterny, K., Paluch, M., Grzybowska, K., Grzybowski, A. (2004) Test of the dynamic lattice liquid model of glass-forming liquids Journal of Molecular Liquids, 109(3), 137-141.

[15] Simha, R., Somcynsk.T (1969) On Statistical Thermodynamics of Spherical and Chain Molecule Fluids Macromolecules, 2(4), 342-&.

[16] Simha, R. (1995) Polyblends-95, in NRCC/IMI Symposium,

[17] Simha, R. (1996) Polymer and oligomer melts: Thermodynamics, correlations, and lattice-hole theory Polymer Engineering and Science, 36(12), 1567-1573.

[18] Yahsi, U. (1999) Journal of Polymer Science Part B-Polymer Physics, 37, 879-887.

[19] Yahsi, U., Ulutas, K., Tav, C., Deger, D. (2008) Journal of Polymer Science Part B-Polymer Physics, 46, 2249-2254.

[20] Yahsi, U., Sahin, F. (2004) Rheologica Acta, 43, 159-167.

[21] Prevosto, D., Capaccioli, S., Lucchesi, M., Leporini, D., Rolla, P. (2004) Journal of Physics-Condensed Matter, 16, 6597-6608.

[22] Casalini, R., Paluch, M., Psurek, T., Roland, C.M. (2004) Temperature and pressure dependences of the structural dynamics: an interpretation of Vogel-Fulcher behavior in terms of the Adam-Gibbs model Journal of Molecular Liquids, 111(1-3), 53-60.

[23] Schwartz, G.A., Tellechea, E., Colmenero, J., Alegria, A. (2005) Correlation between temperature-pressure dependence of the alpha-relaxation and configurational entropy for a glass-forming polymer Journal of Non-Crystalline Solids, 351(33-36), 2616-2621.

[24] Tammann, G., Hesse, W., Anorg., Z. (1926) Allg. Chem., 156 245.

[25] Adam, G., Gibbs, J.H. (1965) J. Chem. Phys., 28 139.

[26] Paluch, M., Roland, C.M., Gapinski, J., Patkowski, A. (2003) Pressure and temperature dependence of structural relaxation in diglycidylether of bisphenol A Journal of Chemical Physics, 118(7), 3177-3186.

[27] Glasstone, S., Laidler, K.J., Eyring, H. (1941) The theory of rate processes; the kinetics of chemical reactions, viscosity, diffusion and electrochemical phenomena, McGraw-Hill Book Company, inc., New York; London.

[28] Ree, T.S., Ree, T., Eyring, H. (1964) Journal of Physical Chemistry, 68, 3262-3268.

[29] Zoller, P., Walsh, D.J. (1995) Standard Pressure-Volume-Temperature Data for Polymers, Technomic Pub. Co., Lancaster, PA.

[30] Schwartz, G.A., Colmenero, J., Alegria, A. (2007) Dielectric study of the segmental relaxation of low and high molecular weight polystyrenes under hydrostatic pressure Journal of Non-Crystalline Solids, 353(47-51), 4298-4302.

[31] Corezzi, S., Capaccioli, S., Casalini, R., Fioretto, D., Paluch, M., Rolla, P.A. (2000) Chemical Physics Letters, 113-117.

[32] Paluch, M. (2001) Effect of temperature, pressure and volume on long time relaxation dynamics in fragile glass-forming liquid Journal of Chemical Physics, 115(21), 10029-10035.

[33] Sahin, F., Tav, C., Yahsi, U. (2006) Int J Thermophys, 27, 1501-1514.

[34] Jain, R.K., Simha, R. (1989) Theoretical Equation of State - Thermal Expansivity, Compressibility, and the Tait Relation Macromolecules, 22(1), 464-468.

RESUME

RESUME			
Name Surname	ASEEL ALMASHAYEK		
Language skills	Arabic, Turkish, English		
Educational Background	**Start Date**	**End Date**	**Name of Institution**
High School	09.2004	07.2007	Pioneer Educational School/Scientific section
Bachelor	10.2004	06.2008	Hashemite University
Master of Science	09.2020	06.2023	Marmara University
Work Experience			**Company Name**
Lab supervisor and teacher	2015	2016	Delta International School
Nuclear department chef	2010	2011	King Hussein Cancer Center
Lecturer	2009	2010	Alkhwarezmi Collage
Publications:	Relaxation Time of PVAc in Terms of Free Volume Fraction Computed from Simha Somcynsky Theory (submitted)		