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Chapter 6. Equations of state and free volume content

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Abstract

The chapter traces the early development of the equation of state concept from the empirical work on condensed gases, to Lennard-Jones and Devonshire approach for gases and liquids. Later, Prigogine proposed the cell model for linear *s*-mer linear molecules. Next, Simha and Somcynsky introduced holes into the cell lattice model obtaining the Helmholtz free energy and derivative functions for small molecule and polymeric liquids, which contained the direct measures of the free volume. The Simha-Somcynsky cell-hole theory is valid for a variety of liquids and glasses, non-polar or polar. However, the Chapter mainly focuses on the use of the theory for neat polymers and multicomponent polymeric systems, such as blends, composites, foams and nanocomposites in the molten state, where the thermodynamic equilibrium conditions are obeyed, as well as in the glassy state where they are not. Finally, the use of the theory for description of thermodynamic non-equilibrium behavior (*e.g.*, transport properties, kinetics of volume relaxation, physical aging, and others) is briefly described.

6.1 Equations of state (eos)

The aim of this chapter is to outline the evolution of the equation of state from the ideal gas to molten and glassy polymers and polymeric systems. After this general background, the basic assumptions of the Simha-Somcynsky (S-S) statistical thermodynamic theory and its broad range of applications are summarized. This hole-cell theory, with its explicit free volume parameter, has been used to describe the configurational thermodynamics of fluids, including the cohesive energy density, surface tension, or entropy. However, the theory is widely known from its equation of state (eos), originally derived for single component liquids and later extended to multicomponent polymeric systems in their molten or vitreous state. The Chapter discusses briefly most of these applications. Furthermore, in this book the use of the S-S eos for the analysis of the positron annihilation lifetime spectroscopy (PALS) is discussed in four Chapters of Part 3, for describing the surface tension in Chapters 8, for analyzing glassy and molten polymeric nanocomposites in Chapter 15 and for describing the flow properties in Chapter 18.

6.1.1 Historical evolution of empirical and semi-empirical equations of state

Any mathematical relation between pressure, P , volume, V , and temperature, T , belongs to the family of equations of state [Thewlis, 1961; Sengers *et al.*, 2000]. Considering the diversity of substances of interest to science (*e.g.*, plasma, nuclear matter, Fermi gas, supercooled or superheated gases, crystalline solid, real gases, liquid solvents, molten polymers, *etc.*) it is predictable that their PVT behavior and corresponding eos will differ considerably. This section provides a short overview of gas-&-liquid eos, which in turn evolved into models attempting to describe the behaviors of increasingly complex substances.

The Boyle's ideal gas law states: “*for any given mass of gas (m), the volume varies inversely with the pressure, provided the temperature is held constant*”, *i.e.*, when m and T are constant so is the product PV . Robert Boyle (1627-1692) developed this rule based on data obtained by utilizing the newly invented thermometers and manometers. Next, Jacques Charles (1746-1823) carried out isobaric experiments, summarized in 1787 as $V/T = \text{constant}$ (when m and P are constant). The isochoric tests of Joseph Louie Gay-Lussac in 1802 led to the “ideal gas law”:

$$PV = nRT \quad (6.1)$$

where R is the gas constant. Deviations from this dependence by real gases inspired Clausius [1880] to formulate the first “realistic” eos:

$$P(V - nb) = nRT \quad (6.2)$$

where b represents *co-volume*, i.e., the volume of gas under extreme pressure, a precursor of the occupied volume in the later theories. Thus, Clausius is credited with introduction of the free volume concept into eos.

Van der Waals (1837-1923) in his PhD thesis [1873] proposed a semi-empirical, two-parameter eos:

$$\left(P + \frac{an^2}{V^2} \right) (V - nb) = nRT \quad (6.3a)$$

where a is a measure of interactions, and b of the “excluded volume”, or what often has been referred to as attractive and repulsive interaction parameters, respectively. The Van der Waals (VDW) cubic ($P \propto V^{-3}$) Eq. (6.3a) might be written in reduced variables, indicated by tilde:

$$\begin{aligned} (\tilde{P} + 3/\tilde{V}^2)(3\tilde{V} - 1) &= 8\tilde{T} \quad \text{or} \quad \tilde{P} = (3\tilde{V} - 2)/\tilde{V}^3 \quad \text{where :} \\ \tilde{V} &\equiv V/V^* ; \quad \tilde{T} \equiv T/T^* ; \quad \tilde{P} \equiv P/P^* \\ V^* &= 3b; \quad T^* = 8a/27Rb; \quad P^* = a/27b^2 \end{aligned} \quad (6.3b)$$

Casting the eos into reduced variables implies commonality of behavior for all fluids, e.g., common $\tilde{P}\tilde{V}\tilde{T}$ surface, or the common value of compressibility at the critical point: $P^*V^*/RT^* = 3/8$. This commonality is known as the corresponding states principle (CSP), which will be discussed later. Since Eq. (6.3) is general, so is the critical point. Thus, originally for the low molecular weight gases and liquids its experimental critical coordinates, P_c , V_c and T_c , were used as the characteristic reducing parameters.

The VDW eos performs much better than the ideal gas law, but it only approximates the real gas behavior. The frequent criticism focused on the a and b parameters – if they are considered

independent of P and T , then the second virial coefficient would be a monotonic function of T . In his Nobel Lecture on 12.12.1910 van der Waals said: “*It will be abundantly clear from my earlier comments that I never expected this equation, with a and b assigned a constant value, to give results numerically in agreement with experiment and yet people almost always thought as that were my opinion.*” VDW also noted that $a = a(T)$ and $b = b(T, V)$. The variability of a and b parameters is especially strong at high P , away from the critical point, where experimentally it might lead to: $V < b$ whereas theoretically $V \gg b$ was assumed. Free-volume is therefore implicit in the VDW eos, where molecules with quantified “excluded volume” are moving inside an unoccupied volume ($V_f = V - V_o$) with uniform potential. The concept of the free volume, or more precisely the free volume fraction, $f = V_f / V$, has been fruitful in physics of the liquid and vitreous state. Detailed methods of computation of the occupied volume, V_o , from the chemical structure have been developed by Bondi [1968], van Krevelen [1997], Porter [1995], and might be extracted from the positron annihilation lifetime spectroscopy (PALS), *e.g.*, see Chapter 11 in this book.

It is fascinating to follow the iterations that started in the 17th century that are still being refined in our time. Over the years numerous authors modified the VDW eos, *e.g.*, Redlich and Kwong [1949], Soave [1972], Peng and Robinson [1976], Patel and Teja [1982], or Schwartzentruber and co-workers [1989]. Their relations, written as $P = P(V, T)$ are known as “cubic” eos, which are algebraically simple and relatively accurate [Valderrama and Alfaro, 2000; Wei, 1998]:

$$P = \frac{RT}{V-b} - \frac{a_c \alpha(T)}{V(V+d) + c(V-d)} \quad (6.5)$$

Depending on the author(s), the parameters d and c , as well as the functions a_c and $\alpha(T)$ take on different meaning or value. Carnahan and Starling [1972] eos incorporates improved rigid-spheres equation that changed VDW parameters a and b :

$$P = RT \left(1 + y + y^2 - y^3 \right) / \left[V (1 - y)^3 \right] - a / V (V + b) T^{1.2}; \quad y \equiv b / 4V \quad (6.6)$$

In a short note, Guggenheim [1965] focused on the repulsive VDW parameter, b , proposing:

$$PV / RT = -a / RTV + (1 - y)^4; \quad y = b / 4V \quad (6.7)$$

The dependence is significantly better than is VDW eos, especially at high fluid density. Other proposed modifications of the VDW eos worth mentioning are: (i) the Berthelot equation; (ii) the Dieterici exponential dependence that leads to $P^*V^*/RT^* \approx 0.272$ correct for non-polar gases, and (iii) a simplified equation, $(P + p_i)(V - V_o) = nRT$ [with the “internal pressure”, p_i], good for low-density fluids, but inadequate for polymer melts [Spencer and Gilmore, 1949, 1950]. In Chapter 8 of this book, Kammer and Kressler cast S-S eos in form of the VDW Eq. (6.3) with the interaction parameters given as functions of the reduced cell volume.

Several types of eos are modifications of the VDW equation with different expressions for the attractive and repulsive interactions. Most authors focused on either a or b . However, Ihm, Song and Mason (ISM) used a statistical mechanical perturbation method with the intermolecular pair potential to obtain a VDW-type eos [Song and Mason, 1989, 1990, 1992; Ihm *et al.*, 1991]:

$$\begin{aligned} VDW : \quad \frac{PV}{RT} &= 1 - \frac{2V - b}{V - b} - \frac{a}{VRT} \\ new : \quad \frac{PV}{RT} &= 1 - \frac{a_n - A_2}{V + 0.22\lambda b_n} - \frac{a_n}{\lambda b_n - V} \end{aligned} \quad (6.4)$$

where the subscript “ n ” indicates parameters of the new ISM eos, A_2 is the second virial coefficient, while λ is a function of the second and third virial coefficients. All three factors, a_n , b_n , and A_2 depend on T .

Other popular semi-empirical, multi-parameter eos is the virial-type [Jacobsen *et al.*, 2000; Carnahan and Starling, 1969; Carnahan and Starling, 1972]:

$$PV / RT = 1 + \sum_{i=1}^n [a_i(T) / V]; \quad a_i(T) = \sum_{j=0}^i (b_{ij} / T) \quad (6.8)$$

and that proposed by Benedict, Webb and Rubin (BWR) [Benedict *et al.*, 1940]:

$$PV = RT + \left\{ \frac{RT(B + b/V) - (A + a/V - a\alpha V^{-4})}{- [C - c(1 + \gamma/V^2 \exp\{-\gamma/V^2\})/V] T^{-2}} \right\} / V \quad (6.9)$$

where a, b, c, A, B, C, α and γ are experimental parameters. The latter one was found useful for description of the PVT behavior of hydrocarbons [Opfell *et al.*, 1959] as well it correctly represents data generated by molecular dynamics (MD) and Monte Carlo (MC) simulations for the L-J fluid [Nicolas *et al.*, 1979; Johnson *et al.*, 1993]. With eight parameters Eq. (6.9) belongs to multi-parameter eos', along with Jacobsen [1972] eos for N_2 with 32 parameters, or UNESCO eos for seawater with 41 parameters [Unesco, 1981; Jackett and McDougal, 1995].

For polymeric PVT data, the preferred empirical representation is the relation proposed by Tait [1889] for the isothermal seawater density at high pressures. Nanda and Simha [1964a] cast it into the form of reduced variables:

$$\begin{aligned} \tilde{V}(\tilde{P}, \tilde{T}) / \tilde{V}_o(0, \tilde{T}) &= 1 - C \ln[1 + \tilde{P} / \tilde{B}(\tilde{T})] \\ \text{where : } C &\cong 0.0894; \\ \tilde{V}_o C &= (\partial \tilde{P} / \partial \tilde{V})_{\tilde{T}} / (\partial^2 \tilde{P} / \partial \tilde{V}^2)_{\tilde{T}}; \quad \text{and} \quad \tilde{B} = -\tilde{V}_o C (\partial \tilde{P} / \partial \tilde{V})_{\tilde{T}} - \tilde{P} \end{aligned} \quad (6.10)$$

The characteristic reducing variables are defined as:

$$\left. \begin{aligned} P^* &= zq\epsilon^* / (sv^*) \\ T^* &= zq\epsilon^* / (Rc) \\ V^* &= v^* / M_s \end{aligned} \right\} \left\{ \begin{aligned} (P^* V^* / RT^*) M_s &= c / s \end{aligned} \right. \quad (6.11)$$

where $zq = s(z-2)+2$ is the number of interchain contacts between s segments (each of molecular weight: $M_s = M_n/s$) in a lattice of the coordination number z , and $3c$ is the number of the external degrees of freedom. Eq. (6.10) does not have correct limits; at high-pressure $\tilde{P} / \tilde{B} \rightarrow \infty$ the specific volume $V < 0$. The reducing parameters are either empirical, or taken from a valid theory. The bulk modulus, $B(T)$, is considered independent of P , and for polymeric melts and glasses, C has a universal value. However, the zero-pressure isotherm $V(0, T)$ and the Tait parameter $B(T)$ must be measured and expressed, *e.g.*, in the form of exponential dependence with two parameters: $F(T) = F_o \exp\{F_1 T\}$ [Quach and Simha, 1971]. Thus, at least four empirical parameters are needed, but since often, the simple exponential is insufficient,

expressions that are more complex had to be used. Several modifications of the Tait dependence have been published [Chang *et al.*, 1996; Sun *et al.*, 1992].

This concludes the short review of the empirical and semi-empirical eos. Interest in them remains strong, especially in the petroleum and foaming industries. Excellent summary and evaluation of diversity of eos was provided by Henderson [1964] and more recently by Sandler [1994]. The theoretically derived eos will be discussed further in the text.

6.1.2 The corresponding states principle (CSP)

Guggenheim started his article on CSP with the sentence: “*The principle of corresponding states may safely be regarded as the most useful byproduct of van der Waals’ equation of state. Whereas this equation of state is nowadays recognized to be of little or no value, the principle of corresponding states correctly applied is extremely useful and remarkably accurate*” [Guggenheim, 1945]. The usefulness of CSP rests in the reduction of great diversity of material behaviors to universal dependencies in form of a constitutive equations written in reduced variables.

Thus, for example, for reduced compressibility the VDW Eq. (6.3) might be written as:

$$\tilde{P}\tilde{V}/\tilde{T} \equiv \tilde{Z} = \tilde{Z}(\tilde{V}, \tilde{T}) \quad (6.12)$$

This CSP expression is obeyed by noble gases, low molecular weight *n*-alkanes, *etc.* CSP derived from ISM is given in Eq. (6.6), but deviations for polar gases (*e.g.*, CO) or polyatomic molecules have been noted. In a series of papers Pitzer and his colleagues proposed generalization of the CSP rule by writing $\tilde{Z}$ in two parts, the first expressing the behavior of the spherical force field molecules, the second “measuring” the deviation from it [Pitzer, 1939; Pitzer and Hultgren, 1958; Pitzer and Brewer, 1961; Danon and Pitzer 1962]:

$$\tilde{Z} = \tilde{Z}^o + \omega\tilde{Z}^1 \quad ; \quad -\omega_\alpha = 1 + \log(\tilde{P}^{sat})_{\tilde{T}=0.7} \quad (6.13)$$

The ω_α , known as the acentric factor, is a function of the reduced saturated vapor pressure $\tilde{P}^{sat} \equiv P^{sat}/P^*$ determined at $\tilde{T} = 0.7$. CSP is obtained for any constant value of the acentric

factor, but for polar, associating liquids more complex expressions are needed [Smith and Van Ness, 1959; Maeso and Solana, 1997; Pai-Panadiker *et al.*, 2002; Kiselev and Ely, 2003; Queimada *et al.*, 2003; Polyakov *et al.*, 2007]. The theoretical analyses lead to the following set of reducing variables [Guggenheim, 1945; Hirschfelder *et al.*, 1954]:

$$P^* = \sigma_{L-J}^3 / \varepsilon \quad T^* = R / \varepsilon; \quad V^* = 1 / \sigma_{L-J}^3; \quad \mu^* = (\varepsilon \sigma_{L-J}^3)^{1/2}; \quad l^* = 1 / \sigma_{L-J} \quad (6.14)$$

where μ^* and l^* are reducing variables for dipole moment and length of “cigar-like” molecules, respectively. It is noteworthy that the L-J parameters, the maximum attractive energy, ε , and the segmental repulsion radius, σ_{L-J} , determine the magnitude of all five variables in Eq. (6.14).

Originally, the L-J potential had a general form [Lennard-Jones, 1929, 1931; Lennard-Jones and Devonshire, 1937]:

$$\phi_o = \lambda_{repulsive} r^{-m} - \lambda_{attractive} r^{-n}; \quad m = 10 \text{ to } 13; \quad n = 6 \text{ or } 7 \quad (6.15)$$

selected for its satisfactory description of gas second virial coefficient with $m, n > 4$. Later, quantum mechanics derivation yielded: $n = 6$ and 7 for attractive forces between H-H and He-He atoms, respectively. The exponent for the short-range repulsive interactions was taken as $m = 2n$, what lead to the general adoption of $n = 6$ and $m = 12$. Over the years, the 6-12 potential was applied to many condensed systems, quite different from gases considered by L-J:

$$E_o(r) = 4\varepsilon \left[A \left(\frac{\sigma_{L-J}}{r} \right)^{12} - B \left(\frac{\sigma_{L-J}}{r} \right)^6 \right] \quad (6.16a)$$

In the statistical thermodynamic derivation of the eos L-J, potential is usually written as:

$$E_o = (qz\varepsilon^*/s) \left[A \left(\frac{v}{v^*} \right)^{-4} - 2B \left(\frac{v}{v^*} \right)^{-2} \right]; \quad v^* = 2^{1/2} \sigma_{L-J}^3 \quad (6.16b)$$

The coefficients $A = 1.011$ and $B = 1.2045$ are for the most commonly assumed face-centered cubic lattice with the coordination number $z = 12$. For polymers, Prigogine *et al.* used the mean-field Eq. (6.19b) to describe interactions between statistical segments of s -unit molecules, with

the radius, r , replaced by cell volume, v [Prigogine and Mathot, 1952; Prigogine *et al.*, 1953a, 1953b, and 1957a,b].

The PVT data for polymer liquids, are “reduced” to dimensionless variables by means of the P^* , V^* , and T^* characteristic parameters defined in Eq. (6.11). It is most satisfying that for molten or glassy polymers the CSP is obtained as an eos in reduced variables.

6.1.3 Cell and holes models

Liquids might be regarded as distorted crystalline solids without the long-range order. This idea originates from the similarity of X-ray diffraction patterns below and above the melting point. More recent MC computations of the density fluctuations (at intermolecular distances) also support this notion [Glasstone *et al.*, 1941; Eyring *et al.*, 1982]. VDW first used such a semi-ordered model assuming that each molecule moves in a cell formed by all other molecules. In terms of L-J scaling factors, VDW cell volume is made off the molecular hard-core, $b = v_0 = 2\pi\sigma_{LJ}^3/3$, and the excluded or free volume, $v_f = v - v_0$, while the attractive interaction parameter is $a = \epsilon v_0$ [Lennard-Jones, 1929, 1931]. The cell model provided good accuracy for condensed fluids, where the intermolecular distance is comparable to the lattice size. The deviation progressively increased with T , which increased the cell size and the lattice distortion [Prigogine, 1953a]. Nanda and Simha [1964b,c] used cell model with 6-12 potential to derive the Helmholtz free energy, $\tilde{F}$, as well as eos, and other thermodynamic functions in reduced variables. The authors found that the predicted $\tilde{V}$ vs. $\tilde{T}$ at $\tilde{P} \approx 0$ deviates at higher T .

The cell model for fluids evolved from VDW to Eyring *et al.* and to Lennard-Jones and Devonshire. The latter authors provided solid basis for the model, introducing clearly defined lattice geometry and interactions, followed by calculation of thermodynamic properties from explicit relations. Thus, each molecule was confined to a cell, each cell was occupied, all neighbors were at a distance a , and the potential energy was spherically symmetrical, given by the 6-12 potential. Inherent to the model is the presence of free volume. As pointed out by Kirkwood [1950], Rowlinson and Curtiss [1951] and later by Hirschfelder *et al.* [1954], there are inherent inconsistencies related to the “communal entropy”, since locking individual molecules in rigid cells reduced the entropy for low density systems by a factor of e^N .

This problem could be avoided by adopting a model with some of the lattice sites left empty, thus introducing holes [Cernuschi and Eyring, 1939; Eyring and Marchi, 1963]. The new lattice model assumed presence of $B \geq N$ cells of constant volume of which only N -cells are occupied by N molecules. Furthermore, as the temperature increases the volume of the cell may stay constant and their number increase, or both the cell size and their number may change with T and P . Assumption of the unoccupied cells solved problem of the “communal entropy” and lead to the “significant structure theory” [Eyring *et al.*, 1958; Eyring and Ree, 1961]. These authors visualized liquids as mixtures of solid-like molecules (occupied lattice sites) and gas-like entities represented by holes. The theory well predicted the critical constants for gases and vapors, but owing to number of empirical parameters, it could not be written in reduced form. The predictive ability of the early cell-hole theories was modest [Rowlinson, 1951].

Peek and Hill (PH) [1950] used the close-packed lattice with $z_0 = 12$ and the nearest neighbor distance a . The N molecules were distributed between B lattice sites; hence the occupied volume fraction was $y = N/B$, and the holes fraction $h = 1 - y$. The interaction energy was introduced via the quasi-chemical equation. Unfortunately, the h -fraction did not explicitly entered the partition function and derived from it free energy. Instead, the authors introduced an expandable lattice parameter: $\alpha = (\sigma_{L-J}/a)^3$, where σ_{L-J} is the L-J scaling parameter. Next, they minimized the Helmholtz free energy, F , with respect to α , what established the number of holes at the thermodynamic equilibrium. The resulting eos was in form of coupled relations, the first derived by minimization, *viz.* $\partial F/\partial \alpha = 0$, the second expressing PV/RT as an algebraically complex integral equation that had to be solved numerically. The new eos performed significantly better than VDW or L-J relations.

6.1.4 Prigogine, Trappeniers and Mathot (PTM) eos for *s*-mers

Most so far discussed eos' concern gases or vapors of small molecules with nearly spherical force field, inherited from the early work by L-J. However, long chain molecules cannot be approximated by spheres. PTM developed the cell model with L-J potential for chain molecules, *e.g.*, high molecular weight *n*-paraffins. These were named by the authors “*r*-mer molecules”, but for the sake of consistency of this book notation, the molecular segments will be called *s*-mers. PTM also noted that lattice imperfections could be accounted for by introduction of holes

[Prigogine, 1953a, 1953b, 1957a,b]. The s -mer molecules are composed of s -segments, or s -mers, each interacting according to L-J potential with all its neighbors. The cell volume is $v = \gamma a^3$, and the number of nearest neighbors is $zq = s(z-2) + 2$. As for small molecule liquids or condensed gases, the arrangement of cells is quasi-crystalline. The molecular energy has two contributions to the partition function: (1) smeared L-J type of intermolecular interactions between point-center of a s -mer and all its neighbors, and (2) intramolecular term originating from deformation of the s -mer; both might be approximated either by a harmonic oscillatory fields, or by square-well potential (SWP). For the former case, the molecule was represented by an assembly of $3s$ linear harmonic oscillators with potential given by:

$$\phi(r) - \phi_o = \phi_o s^2 / (a - \sigma)^2 \quad (6.17)$$

where ϕ_o is the potential energy when the point s -mer is in the cell center. The total partition function, $\psi'(s)$, is a sum of the internal part, Z_o , and the volume dependent part, $\psi(s)$:

$$\psi'(s) = Z_o + \psi = \sum_{i=1}^{n-p} (k_B T / h \nu'_i) + (k_B T / h \nu)^{s+3} \quad (6.18)$$

with ν_i being the oscillators' frequency and k_B is the Boltzmann constant. For linear molecules, introduction of simplified L-J potential for harmonic field gave:

$$\nu = \sqrt{2\phi_o / m(a - \sigma)^2} / 2\pi \quad (6.19)$$

where m is the mass per cell, a is the distance between first neighbors sites in the lattice, and σ is the L-J scaling parameter. The resulting eos has the form:

$$\begin{aligned} \tilde{P}\tilde{V} / \tilde{T} &= \left(1 - 0.8909\tilde{V}^{-1/3}\right)^{-1} - 6(A\tilde{V}^{-2} - B) / (A\tilde{V}^{-2} - 2B) + (A\tilde{V}^{-4} - B\tilde{V}^{-2}) / \tilde{T} \\ \tilde{T} &= k_B T (1 + s/3) / 2zq\phi_o; \quad \tilde{V} = V / sNv_o; \quad \tilde{P} = P s v_o / 2zq\phi_o \end{aligned} \quad (6.20)$$

The eos was used for correlating the specific volume of a homologous series of n -paraffins, viz. CH₄ with $s = 1$; C₃H₈, $s = 2$; and C₅H₁₂, $s = 3$, since $\sigma(\text{CH}_4) = 0.422$ nm, is comparable to that of CH₃-CH₂ or CH₂-CH₂.

The work on s -mers resulted in development of the CSP theorem and related to it definition of the external degrees of freedom, c – four types of s -mer chain were considered [Prigogine *et al.*, 1957a; Bellemans *et al.*, 1957a,b]:

1. rigid, where $c = 5$ or 6 , and for $s \rightarrow \infty$, $3c/s = 0$,
2. semirigid, where: $3c = s + 3$, and for $s \rightarrow \infty$, $3c/s = 1$,
3. flexible, where: $3c = 2s + 1$, and for $s \rightarrow \infty$, $3c/s = 2$, and
4. rigid sphere, where: $3c = 3s$, and $3c/s = 1/3$, independent of size.

The derived reducing parameters, P^* , T^* and V^* are equivalent to those presented in Eq. (6.11), with the number averaged molecular weight, $M_n = sM_s$. The authors demonstrated that the theorem is valid for the L-J potential, harmonic potential, or SWP.

Many authors modified the PTM cell model. For example, Nanda and Simha [1964b] followed the original derivation but instead of the harmonic potential, they used SWP, deriving:

$$\begin{aligned} \tilde{P}\tilde{V}/\tilde{T} &= \left(1 - 2^{-1/6} \tilde{V}^{-1/3}\right)^{-1} + 2(A\tilde{V}^{-4} - B\tilde{V}^{-2})/\tilde{T} \\ \tilde{T} &= ck_B T / zq\varepsilon^*; \quad \tilde{V} = V/V^*; \quad \tilde{P} = PV^*/zq\varepsilon^*; \quad A=1.011; \quad B=1.2045 \end{aligned} \quad (6.21)$$

The new dependence was algebraically simpler and better described the experimental PVT data than Eq. (6.20), extending the accuracy of $\tilde{V}$ vs. $\tilde{T}$ at $\tilde{P} = 0$ to higher temperatures. DiBenedetto assumed that chain segments interact with a cylindrically symmetric SWP [DiBenedetto, 1963; Paul and DiBenedetto, 1967]. The modifications by the Flory, Orwoll, and Vrij (FOV) [1964] and by Dee and Walsh [1988a,b] will be discussed in the following part.

More recently, Arora *et al.* [2001] re-derived eos starting with Prigogine *et al.* cell model and full L-J potential:

$$\tilde{P}\tilde{V}/\tilde{T} = 1 + (4/\tilde{T})[F_L/\tilde{V}^4 - F_M/\tilde{V}^2] + (2/\tilde{T})[A/\tilde{V}^4 - B/\tilde{V}^2] \quad (6.22)$$

The reduced variables are defined in terms of the L-J scaling parameters, ε^* and v^* , while the numerical values of integrals F_L and F_M are tabulated. The above dependence describes the behavior of condensed systems where $h \rightarrow 0$. For $P \rightarrow 0$, Eq. (6.22) follows an empirical relation

with adjustable parameters a and b [Simha and Weil, 1970; Simha *et al.*, 1973; Utracki and Simha, 2001a]:

$$\ln \tilde{V} = a + b \tilde{T}^{3/2} \quad (6.23a)$$

The authors used Eq. (6.23a) with different values of a and b parameters for the V - T dependencies in the melt and solid state.

It is noteworthy that Bueche derived a similar, but linear expression for liquid expansion [Bueche, 1962]:

$$V = V_o + (nV_o / 6\pi)(k_B T)^{3/2} \quad (6.23b)$$

where V_o is the occupied volume, n the number of molecules in volume V . *Nota bene*, a similar replacement of the linear by logarithmic function was made for viscosity vs. density dependence, first proposed by Batchinski and then by Doolittle [Utracki and Sedlacek, 2007].

6.1.5 Equations of state for polymers

The eos evolved from the early description of the PVT behavior of gas, to liquids, to *s-mer* molecules, and finally to polymers in the molten or vitreous state. The eos is mean field model, unable to account for orientation, local heterogeneities, or phase separation. It best performs in single-phase systems, away from the transition temperatures. There are several mechanisms responsible for structural changes and secondary transitions in molten polymers, which are rarely visible on the PVT surface and unaccounted for by eos [Utracki, 2007].

Several reviews on the topic are available, viz. Curro [1974], Zoller [1989], Rodgers [1993], Rudolf *et al.* [1995, 1996], and Lambert *et al.* [2000]; these outline derivations of selected eos and compare the precisions for describing the experimental PVT results.

From the large number of published eos for polymers, only few will be mentioned in this section. Most are based on the Prigogine cell model, others are semi-empirical or based on the Ising fluid; the smallest group is based on the cell-hole model. One of the reasons for the limited enthusiasm toward the latter models is that “by nature” they are algebraically more complex.

1. DiBenedetto [1963, 1967].

According to the available information, DiBenedetto [1963] was the first who applied the cell model to polymers. He replaced the spherical cells by elongated ones, where segments of macromolecules (about the Kuhn's segment size) had four neighbors. The aligned segments interacted according to L-J potential, with SWP simplification for the cell partition function:

$$PV/T = (3c/2) \left(1 - 0.83\tilde{V}^{-1/2}\right)^{-1} - (\varepsilon^* P^* / \lambda k_B T) (5.81\tilde{V}^{-5/2} - 4.26\tilde{V}^{-11/2}) \quad (6.24a)$$

where l is the segment length. The new model was found to work relatively well for $\tilde{V} \leq 1.1$. In the following publication, an isobaric expression was derived [Paul and DiBenedetto, 1967]:

$$\tilde{V} = \left[0.935 + 10.8(l/\rho^*)^2 \right] + \left[0.824 + 24.9(l/\rho^*)^2 \right] (3c\lambda k_B / 2\varepsilon^* \rho^*) T \quad (6.24b)$$

with three characteristic constants: ε^* = the interactions constant, ρ^* = separation distance between centers of neighboring segments, and l = a measure of segment size. Treating these as adjustable resulted in superposition of the PVT data for organic liquids and polymeric melts.

2. Flory-Orwoll-Vrij (FOV) [1964]

FOV eos was developed to correlate properties of macromolecular liquids, *sacrificing rigor of mathematical derivation for simplicity*. The authors followed Prigogine's derivation up to the configurational partition function, and then modified the expression for the intermolecular energy, E_o . The final product is indeed algebraically simple:

$$\begin{aligned} \tilde{P}\tilde{V}/\tilde{T} &= (1 - \tilde{V}^{-1/3})^{-1} - 1/\tilde{V}\tilde{T} \quad \text{with:} \\ \tilde{V} &= V/V^*; \quad \tilde{T} = T/T^*; \quad \tilde{P} = P/P^* \\ V^* &= \rho_*^3; \quad T^* = s_*\eta_*/(c_*k_B); \quad P^* = c_*k_B T^*/V^* \end{aligned} \quad (6.25)$$

where: ρ_* , s_* , η_* , c_* are respectively: the "hard-sphere" radius, number of contacts per segment, the segment-segment interaction energy, and the coordination number. The dependence was tested on isothermal liquid n -paraffins ($n = 6$ to 40). The authors remarked that the relation is "less satisfactory" over wider range of T and P and that isobars curvature is overestimated.

3. Sanchez-Lacombe (S-L) [1976-8]

Sanchez and Lacombe [1976, 1978] eos is based on the Ising fluid model. The authors followed Guggenheim [1966] approach, placing in a N -lattice: N_r -mers and N_o holes. Hard core volume of the r -mer, as well as its flexibility was assumed independent of T and P . Furthermore, only the nearest neighbors of non-bonded mers contributed to the lattice energy:

$$\begin{aligned}\tilde{P}\tilde{V}/\tilde{T} &= -\tilde{V}[\ln(1-\tilde{\rho}) + (1-1/r)\tilde{\rho}] - 1/\tilde{T} \tilde{V} \\ \tilde{\rho} &= 1/\tilde{V} = V^*/V; \quad \tilde{T} = T/T^*; \quad \tilde{P} = P/P^* \\ \text{where} \quad r &= M_w P^* / RT^* \rho^*; \quad T^* = \varepsilon^* / k_B\end{aligned}\quad (6.26)$$

where M_w is the weight-average molecular weight, ρ^* is the characteristic density parameter. Evidently, the presence of the parameter r negates the CSP – it can be recovered only for $r \rightarrow \infty$. The theory was formulated mainly for describing properties of solvents, solutions, or mixtures. The model is simple, semi-quantitative and easy to modify. One such modification changed the lattice energy term by means of the segmental surface to volume ratio [Panayiotou and Vera, 1982]. The resulting expression for macromolecules ($r \rightarrow \infty$) is:

$$\tilde{P}\tilde{V}/\tilde{T} = -[\ln(1-\tilde{\rho}) + 1] - \theta^2 \tilde{V}/\tilde{T} \quad \text{where} \quad \theta \equiv [1 + S_o(\tilde{V}-1)/S]^{-1} \quad (6.27)$$

In Eq. (6.27) the parameters S and S_o are the number of external contacts of mers and holes, respectively (calculated from the mer chemical structure using Bondi's tabulated data).

Sanchez *et al.* [1993] reported that the plots of the compressional strain, $\ln(V/V_o)$, vs. the reduced pressure, $\Delta P = (P - P_o)/B_o$, are independent of T :

$$\begin{aligned}\ln(V/V_o) &= -\Delta P + \frac{B_1 \Delta P^2}{2!} - \frac{(2B_1^2 - B_o B_2) \Delta P^3}{3!} + \dots \\ \text{where: } \Delta P &= (P - P_o)/B_o = [\rho(\partial F / \partial \ln \rho) - P_o B_o] B_o V_o \quad \text{and} \quad B_o = \lim_{P \rightarrow P_o} B\end{aligned}\quad (6.28)$$

In Eq. (6.28) F is Helmholtz free energy, B is the bulk modulus, and B_o is its isothermal value evaluated at a reference pressure, P_o . An excellent superposition of data was achieved, indicating generality of the relation. In the following paper, Eq. (6.28) in a modified form was used to compute the reducing parameters for 61 polymeric liquids [Sanchez and Cho, 1995].

4. Hartmann and Haque (H-H) [1985].

Hartmann and Haque (H-H) [1985a,b] derived a semi-empirical eos for liquid polymers, starting with the total pressure as $P(V, T) = P_o(V) + T^{3/2}V^{-\gamma}$, expressed as a sum of internal pressure along the $T = 0$ isotherm, and thermal pressure, $P(T, V)$, with the Gruneisen parameter $\gamma = 5$ [Pastine and Warfield, 1974, 1981]. Combining this dependence with Eq. (6.23a) gave:

$$\tilde{P}\tilde{V}^5 = \tilde{T}^{3/2} - \ln \tilde{V}, \text{ with: } \tilde{V} = V/V_0; \quad \tilde{T} = T/T_0; \quad \tilde{P} = P/B_0 \quad (6.29)$$

The new eos in reduced variables is mathematically simple and well represents the PVT behavior of molten polymers. The pressure reducing parameter, B_0 , has been identified as the isothermal bulk modulus extrapolated to $T = 0$ and $P = 0$.

5. Dee and Walsh (D-W) [1988].

Dee and Walsh [1988] derived the most successful modification of the Prigogine's model as the "modified cell model" (MCM). The basic idea is that due to limited temperature range where molten polymer may exist (from the glass transition temperature, T_g , or melting point, T_m , to the degradation temperature, T_d) the suitable eos should be formulated for dense liquids. As earlier authors, D-W also used the L-J potential and SWP. To improve the eos performance the authors decoupled free volume, $V_f = [V^{1/3} - q(V_{hc})^{1/3}]^3$, where $q \approx 1.07 \pm 0.02$ is a numerical factor (for seven polymers: $q = 1.044 - 1.083$), $V_{hc} = \chi V^*$ is the hard-core cell volume with $V^* = \sigma^3$ and $\chi = Va^{-3}$ dependent on cell geometry. The MCM in dimensionless variables is:

$$\begin{aligned} \tilde{P}\tilde{V}/\tilde{T} &= (1 - 2^{-1/6}q\tilde{V}^{-1/3})^{-1} + (2/\tilde{T})(A\tilde{V}^{-4} - B\tilde{V}^{-2}) \\ \tilde{V} &= V/V^*; \quad \tilde{T} = T/T^*; \quad \tilde{P} = P/P^* \\ q &\cong 1.07; \quad A = 1.011; \quad B = 1.2045 \end{aligned} \quad (6.30)$$

The dependence would be identical to that of Nanda and Simha Eq. (6.21) if not for the correction to hard-core cell volume, the parameter q .

6. Reviews of the eos for polymer melts

There are many publications comparing different eos to each other, and few more ambitious reviews, which discuss their derivation and application, fundamentals of theories, and provide tabulated characteristic reducing parameters as well as differences between the experimental and computer volumes [Curro, 1974; Zoller, 1989; Rodgers, 1993; Rudolf *et al.*, 1995, 1996; Lambert, 2000]. For example, Zoller [1989] examined eos by Spencer-Gilmore (S-G) [1949, 1950], Flory-Orwoll-Vrij (FOV), Sanchez-Lacombe (S-L), and Simha-Somcynsky (S-S). Large deviations (≤ 0.01 mL/g) were observed for S-G. FOV and SL expressions were useful at low P . The S-S eos consistently provided the best representation of data over extended ranges of T and P , with deviations $\Delta V \leq 0.003$ mL/g, comparable to the experimental error for density.

Table 6.1. Global-average difference between the experimental and calculated volume of 56 polymers, $\pm \Delta V$ ($\mu\text{L/g}$) [Rodgers, 1993].

Authors (chronologically)	eos	Pressure range (MPa)	
		0 – 50	0 – 200
Prigogine <i>et al.</i> , 1957a	CM	0.6	0.8
Flory-Orwoll-Vrij, 1964	FOV	0.7	2.2
Simha-Somcynsky, 1969	S-S	0.4	0.7
Sanchez-Lacombe, 1976-8	S-L	1.0	3.3
Hartman-Haque, 1985	H-H	0.6	0.9
Dee-Walsh, 1988	D-W	0.5	0.6

Rodgers [1993] collected PVT data for 56 polymers at $P \leq 200$ MPa and T -span of 50 to 150°C. Table 6.1 summarizes his findings. Within the low-pressure region all eos (but S-L) show similar deviations from the experimental data: $\Delta V \approx 0.4 - 0.7$ ($\mu\text{L/g}$). Within the full pressure range, S-L and FOV performed poorly, while S-S and D-W continued to provide good description. Surprisingly, CM in the form given by Eq. (6.21) performed well. Rudolf *et al.* [1995, 1996] confirmed these observations.

6.2 Simha-Somcynsky statistical thermodynamics of chain molecules

The hole theories have been developed as improvements over the cell models. Similarly as in Ising fluid model, holes were placed on the lattice. Their presence cured the problem of the common entropy, and by introducing a degree of disorder in the pseudo-crystalline lattice, improved the description of liquid behavior at higher T . The lattice cell volume was assumed constant, independent of T and P [Sanchez and Lacombe, 1976, 1978].

The Simha and Somcynsky (S-S) [1969] cell-hole theory is based on the lattice-hole model. The molecular segments of an s -mer occupy y -fraction of the lattice sites, while the remaining sites, $h = 1 - y$, are occupied by randomly distributed holes. The fraction h is a measure of the free volume content. The goal was to provide improved description of fluids, ranging from low molecular weight “spherical” molecules (such as argon) to macromolecular chains.

The S-S configurational partition function is:

$$\begin{aligned} Z &= g(N, y) \left[v_f(V, y) \right]^{cN} \exp \{ -E_o(V, y) / k_B T \} \\ g(N, y) &\propto y^{-N} (1 - y)^{-Ns(1-y)/y} \\ E_o(V, y) &= (yNqz\varepsilon^*/2) \left[A(v^*/\omega)^4 - 2B(v^*/\omega)^2 \right]; \quad \omega \equiv yV/(Ns) \end{aligned} \quad (6.31)$$

In Eq. (6.31), the combinatorial factor g is taken from Huggins and Flory theory, and E_o is the L-J potential. The variables were converted to the reduced form defined in Eq. (6.11). Thus, the macromolecules are composed of s segments, each having the molecular weight $M_s = M_n/s$ (M_n is the number-averaged molecular weight) not necessarily equal to the mer molecular weight, M_o . The total number of volume dependent, external degrees of freedom is $3c$, and the number of interchain contacts in a lattice of coordination number $z = 12$ is $qz = s(z-2) + 2$.

The free volume quantity in Eq. (6.31) is a volume-average of the solid-like and gas-like contributions:

$$\tilde{v}_f = \left[y \left(\tilde{\omega}^{1/3} - 2^{-1/6} \right) + (1 - y) \tilde{\omega}^{1/3} \right]^3 \quad (6.32)$$

The assumption implies that both holes and occupied cells contribute to volume changes and that the cell distribution follows SWP. The configurational Helmholtz free energy was obtained as:

$$\begin{aligned}\tilde{F} &= \tilde{F}[\tilde{V}, \tilde{T}, h(\tilde{V}, \tilde{T})] = -RT \ln Z \\ \tilde{F} / k_B T &= N \ln y + sN[(1-y)/y] \ln(1-y) - \\ 3cN &\left\{ \ln \left[(y\tilde{v})^{1/3} - 2^{-1/6} y \right] + Nqz(\varepsilon^* / 2kT) \left[A(y\tilde{v})^{-4} - 2B(y\tilde{v})^{-2} \right] \right\}\end{aligned}\quad (6.33)$$

It is noteworthy that in addition to the usual volume and temperature dependence, $\tilde{F}$ contains the hole fraction $h = 1 - y = h(\tilde{V}, \tilde{T})$.

6.2.1 Simha-Somcynsky equation of state for a single component

Differentiations of the Helmholtz free energy lead to the S-S eos at the thermodynamic equilibrium:

$$(\partial \tilde{F} / \partial h)_{\tilde{T}, \tilde{V}} = 0 \quad \text{and} \quad \tilde{P} = -(\partial \tilde{F} / \partial \tilde{V})_{\tilde{T}} \quad (6.34)$$

The first differential determines the optimum free volume content at constant V and T [Peek and Hill, 1950], while the second is a standard definition of pressure. These yield the S-S eos in the form of coupled equations:

$$\begin{aligned}3c &\left[(\eta - 1/3) / (1 - \eta) - y(3AQ^4 - 2BQ^2) / 6\tilde{T} \right] + (1 - s) - (s/y) \ln(1 - y) = 0 \\ \tilde{P}\tilde{V} / \tilde{T} &= (1 - \eta)^{-1} + 2y(AQ^4 - BQ^2) / \tilde{T}\end{aligned}\quad (6.35)$$

with $Q = 1/(y\tilde{V})$ and $\eta = 2^{-1/6}yQ^{1/3}$. The two equations predict how V and h vary with P and T . The relation between h and the free volume fraction, f , was published by Utracki and Simha [2001a]. The S-S theory also predicts variations of the reduced cohesive energy density, $\tilde{C}\tilde{E}D$, and internal pressure, $\tilde{P}_i$:

$$\begin{aligned}\tilde{C}\tilde{E}D &= \tilde{U} / \tilde{V} = (y / 2\tilde{V}) [AQ^4 - 2BQ^2] \\ (\partial \tilde{U} / \partial \tilde{V})_{\tilde{T}} &= \tilde{P}_i = -\frac{1}{2} [3AQ^4 - 2BQ^2] (\partial y / \partial \tilde{V}) + (2y / \tilde{T}) [AQ^4 - BQ^2]\end{aligned}\quad (6.36)$$

where U is internal energy of the system – one of the intensive thermodynamic quantities. From CED the solubility parameter can be calculated as $\delta = \sqrt{CED} = \sqrt{\tilde{C}\tilde{E}D \times P^*}$. Accordingly, δ is also intensive function: $\delta = \delta(T, P)$, not T -independent quantity as often claimed.

Of all the eos, only the one derived by S-S explicitly gives the hole fraction, $h = 1 - y$, a measure of the free volume fraction, f . Eq. (6.35) provides a corresponding states description of PVT surface of any liquid. Once the characteristic parameters (P^* , V^* , T^* , and $3c/s$) are known, the V , h and all derivative thermodynamic properties may be computed in the full range of P and T . For the linear molecules, the external degrees of freedom are proportional to number of segments: $3c/s = 1 + 3/s$. Thus, for linear polymers, where $s \gg 3$, the external degree of freedom: $3c/s \cong 1$, and only knowledge of P^* , V^* , and T^* is required.

6.2.2 Single component PVT surface

An example of the S-S eos fit to experimental data is shown in Figure 6.1; the theory well represents the test results. However, since it is fitted to the whole region of molten polymers, it smoothes over discrete variability caused by secondary transitions, evident in derivative properties.

Figure 6.1. Results of five PVT tests for PS at $T = 373$ – 517 (K) and $P \leq 190$ MPa. The straight lines indicate limits of the transition region, **T**. Points are experimental, open circles are from the Eq. (6.35).

Figure 6.2. Compressibility parameter for PS; monotonic increase of κ with T is observed only at $T > 1.2T_{g,P=0}$. The transitory behavior at $T_g \leq T \leq 1.2T_g$ is invisible in Figure 6.1.

As shown in Figure 6.2, the compressibility parameter calculated from Figure 6.1 data indicates complex behavior at $T_g \leq T \leq 1.2T_g$ [Utracki, 2008a]; see also Chapter 15 in this book. Evidently, forcing a single equation to describe two regions of the melt behavior introduces deviation – wider is the range of variables larger the deviation might be expected. The accuracy of pressure dilatometry is about 0.02 to 0.03%, the contribution due to fitting data in two regions of different melt structure may double this error. Thus, deviations of $\Delta V = \leq 0.06\%$ might be taken as an indication of adequacy of eos [Utracki, 2007a].

6.2.3 CED of single component

Analysis of CED for 38 molten polymers showed that, in accord with VDW prediction, the product $\delta V \propto (\tilde{U}\tilde{V})^{1/2} \sim \text{const.}$, thus the solubility parameter: $\delta \propto 1/V(P,T)$ depends on the specific volume. Knowing the reducing parameters, δ might be computed from Eq. (6.36) in the full range of T and P . These values are significantly higher than those listed in handbooks are. The discrepancy originates in extra free volume introduced by solvents traditionally used for the determination of δ for polymers; the presence of solvent increases the polymer free volume equivalent to heating it to $T \geq T_g + 300$ K [Utracki, 2004; Utracki and Simha, 2004].

6.3 Modifications of S-S eos

Since publication of S-S eos in 1969 several modifications have been proposed, either to simplify the use of Eq. (6.35), or to explore different theoretical assumptions.

6.3.1 Simplified S-S eos

The first simplification was suggested by Olabisi and Simha [1977]. Combining Tait's Eq. (6.10) with the volume-temperature dependence of S-S eos, Eq. (6.23) and observed linear dependence of the Tait compressibility parameter: $-\ln \tilde{B} = 0.04615 + 49.22\tilde{T}$, the authors wrote:

$$\tilde{V}(\tilde{P}, \tilde{T}) = \left[0.9018 \exp\{23.83\tilde{T}^{3/2}\} \right] \times \left\{ 1.0 - 0.0894 \ln \left[1.0 + 1.047P \exp(49.22\tilde{T}) \right] \right\} \quad (6.37)$$

The three reducing parameters correlated as:

$$\ln(P^*V^*/T^*) = 1.3191 - (3 \times 10^{-4} / 2.01)T^* \quad (6.38)$$

In another simplification $\tilde{V}$ and h were computed for molten polymers from Eq. (6.35) in the full range of independent variables $1.6 < 100 \times \tilde{T} < 7.1$, and $0 < 100 \times \tilde{P} < 35$ [Utracki and Simha, 2001a]. Fitting the obtained data to various five-parameter polynomials resulted in selection of the following dependencies:

$$\ln \tilde{V} = a_0 + a_1 \tilde{T}^{3/2} + \tilde{P} \left[a_2 + (a_3 + a_4 \tilde{P} + a_5 \tilde{P}^2) \tilde{T}^2 \right] \quad (6.39)$$

$$h(\tilde{V}, \tilde{T}) = a_0 + a_1 / \tilde{V} + a_2 \tilde{T}^{3/2} + a_3 / \tilde{V}^2 + a_4 \tilde{T}^3 \quad (6.40)$$

The selection was based on the measures of the goodness of fit: the standard deviation (σ), the correlation coefficient squared (r^2) and the coefficient of determination (C_d). It is noteworthy that the selected range of variables is much wider than that experienced by a single polymer. The Eqs. (6.39) and (6.40) parameters and those of the goodness of fit are listed in Table 6.2.

Table 6.2. Statistics of the polynomial data fit to S-S eos: $\tilde{V} = \tilde{V}(\tilde{T}, \tilde{P})$ and $h = h(\tilde{V}, \tilde{T})$

Parameters	Values for V/V^*	Values for h
a_0	-0.10346 ± 0.00034	1.203 ± 0.020
a_1	23.854 ± 0.032	-1.929 ± 0.047
a_2	-0.1320 ± 0.0012	10.039 ± 0.249
a_3	-333.7 ± 2.5	0.729 ± 0.026
a_4	1032.5 ± 23.6	-218.42 ± 10.29
a_5	-1329.9 ± 52.8	--
σ	0.00183	0.00253
r^2	0.99973	0.99965
C_d	0.99967	0.99899
Comments		most errors at $\tilde{V} \leq 0.93$

Similarly, the scaled $C\tilde{E}D$ and $\tilde{\delta} = \tilde{\delta}(\tilde{T}, \tilde{P})$ were approximated by:

$$\begin{aligned} C\tilde{E}D &= a_o + a_1 / \tilde{V}^2 + a_2 \tilde{T} + a_3 / \tilde{V} + a_4 \tilde{V} \tilde{T} \\ \tilde{\delta} &= a_o + a_1 \tilde{P} / \tilde{T} + (a_2 + a_3 \tilde{P} + a_4 \tilde{P}^2) \tilde{T} \end{aligned} \quad (6.41)$$

Values of the fitting parameters of Eq. (6.41) are listed in [Utracki and Simha, 2001a].

6.3.2 Modified S-S eos

To modify the S-S theory Nies and Stroeks [1990a,b] used Huggins expression for the conformational entropy term, replacing the contact sites by surface site fractions in expressions for the internal energy and the segmental free length. These modifications led to:

$$\begin{aligned} & (3\eta - 1 + \alpha y) / [(1 - \eta)(1 - \alpha y)] - (1 - \alpha) y \left[(3AQ^4 - 2BQ^2) - 4\alpha y (AQ^4 - BQ^2) \right] / \\ & \left[2\tilde{T} (1 - \alpha y)^2 \right] - c_s \left\{ \ln[(1 - y) / y] + \beta - \ln[\beta(1 - \alpha y) / \alpha y] - \beta \right\} = 0 \\ & \tilde{P} \tilde{V} / \tilde{T} = (1 - \eta)^{-1} + 2(1 - \alpha) y (AQ^4 - BQ^2) / \tilde{T}; \quad c_s = 1/3 + 1/s \\ & \beta - 1 - 1/s; \quad \alpha = 2\beta / z; \quad \eta = 2^{-1/6} Q^{1/3} y (1 - \alpha) / (1 - \alpha y) \end{aligned} \quad (6.42)$$

The variables in Eq. (6.42) either are defined there or are the same as in Eq. (6.35). The two eos' offer similar predictions of the PVT behavior, thermal expansion and compressibility. The modification suggests higher free volume content, mainly due to higher number of the external degrees of freedom. The modified Eq. (6.42) provides better prediction of the polymer/solvent miscibility and P dependence of the critical mixing temperature.

Zhong *et al.* [1993] examined the temperature dependence of defects in imperfect crystals. The analysis indicated an exponential increase with T . The authors assumed that $z = 8$. The modifications resulted in "simplified hole theory" (SHT) in form of the coupled expressions:

$$\begin{aligned} y &\cong 1 - \exp\{-0.52 / \tilde{T}\} \\ \tilde{P} \tilde{V} / \tilde{T} &= (1 - 0.9165 Q^{1/6})^{-1} + 2y (1.1394 Q^4 - 1.5317 Q^2) / \tilde{T} \end{aligned} \quad (6.43)$$

Comparison of Eq. (6.35) and Eq. (6.43) fit to PVT data of 11 polymers showed similar average deviations, viz. $\Delta V(\%) = 0.085 \pm 0.020$ and 0.078 ± 0.020 , respectively. The second publication reported similar deviations for polymer solutions and blends [Zhong *et al.*, 1994].

Wang *et al.* [1997] fitted PVT data of 67 liquids to FOV, S-L, Prigogine CM, S-S, and SHT eos. The grand average deviation was, respectively: 0.156, 0.229, 0.084, 0.065, and 0.066, suggesting that indeed S-S and SHT relations lead to similar precision, superior to others eos.

The S-S eos was recently modified to make it more suitable for gases as well as molten polymers in a wide range of P [Wang *et al.*, 2006]. The authors used a modified partition function (from the perturbed hard-chain theory) and expression for the vibrational degree of freedom per molecule. For better fit to low molecular-weight fluids, two constants, a and b , were introduced into the free volume term:

$$3c \left[(ab\eta^* - 1/3) / (1 - b\eta^*) - y(3AQ^4 - 2BQ^2) / 6\tilde{T} \right] + (2 - s - c) - (s/y) \ln(1 - y) = 0$$

$$\tilde{P}\tilde{V} / \tilde{T} = (1 - b\eta^*)^{-1} + 2y(AQ^4 - BQ^2) / \tilde{T} \quad (6.44)$$

where: $\eta^* = 2^{-1/6} y^a (y\tilde{V})^{-1/3}$

The Modified S-S (MSS) eos was used with two sets of the universal parameters: for MSS-I $a = b = 1$, and for MSS-II $a = 1.140$; $b = 1.257$. Owing to redefinition of the degrees of freedom neither MSS-I nor MSS-II reduce to Eq. (6.35). The authors calculated the critical point coordinates, saturated vapor pressure and saturated liquid density for 44 low molecular-weight substances. MSS-II gave better fit than MSS-I with the errors for T_c , P_c and ρ_c , equal respectively: 0.86, 2.38 and 20.5%. The characteristic reducing parameters and the absolute average deviations for the density of 64 polymers were determined for MSS-I, MSS-II and S-S eos. The reported average deviations for all three eos were within the range of good fit to the experimental data, $\Delta V \leq 0.06\%$; hence, the modification did not improve the S-S eos fit to the PVT surface, but probably extended its application to low density systems.

6.4 Multicomponent systems

6.4.1 General

Prigogine *et al.* extended the cell model eos to solutions, [Prigogine and Mathot, 1952] and then to the s -mer mixtures [Prigogine *et al.*, 1953a,b; Prigogine, 1957a,b; Bellemans *et al.*, 1957a,b]. Assuming that in multicomponent fluids there is only one type of vacancies, and one cell size for all components, Jain and Simha [1980, 1984] developed a set of relations for homogeneous, binary mixtures. Based on detailed analysis the authors concluded that the S-S theory is applicable to multicomponent systems, if the reducing and interaction parameters are expressed as composition-dependent averages indicated by the angular brackets, $\langle \rangle$:

$$\begin{aligned} \langle P^* \rangle &= qz \langle \varepsilon^* \rangle / (\langle s \rangle \langle v^* \rangle); \quad \langle T^* \rangle = qz \langle \varepsilon^* \rangle / R \langle c \rangle; \quad \langle V^* \rangle = \langle v^* \rangle / \langle M_o \rangle \\ \langle P^* \rangle \langle V^* \rangle / R \langle T^* \rangle &= (\langle c \rangle / \langle s \rangle) (1 / \langle M_o \rangle) \\ \langle c \rangle &= \sum_i c_i x_i; \quad \langle s \rangle = \sum_i s_i x_i; \quad \langle M_o \rangle = \sum_i M_{si} s_i x_i / \sum_i s_i x_i \end{aligned} \quad (6.45)$$

The interacting site fractions, X_i depend on the lattice interchain contact, zq_i , and the mole fractions x_i :

$$X_i = zq_i x_i / \sum zq_i x_i; \quad zq_i = s_i(z-2) + 2; \quad z = 12 \quad (6.46)$$

The average interaction parameters $\langle \varepsilon^* \rangle$ and $\langle v^* \rangle$ are related to binary ones via:

$$\langle \varepsilon^* \rangle \langle v^* \rangle^m = \sum_{i,k} X_i X_k \varepsilon_{i,k}^* (v_{i,k}^*)^m; \quad m = 2, 4 \quad (6.47)$$

where the two values of m reflect the assumed Lennard-Jones 6-12 potential.

As it will be evident from the examples cited in the following parts, the S-S theory for multicomponent systems has been successful in describing thermodynamics (*e.g.*, phase equilibria, CED, solubility), PVT behavior of polymer mixtures with gases, liquids, or solids.

For binary systems, Eqs. (6.45) and (6.47) might be written as:

$$\begin{aligned} X_1 &= q_1 z X_1 / (q_1 z X_1 + q_2 z X_2); \quad \langle c \rangle = c_1 x_1 + c_2 x_2; \quad \langle s \rangle = s_1 x_1 + s_2 x_2 \\ \langle M_o \rangle &= (M_{s1} s_1 x_1 + M_{s2} s_2 x_2) / (s_1 x_1 + s_2 x_2) \end{aligned} \quad (6.48)$$

and:

$$\langle \varepsilon^* \rangle \langle v^* \rangle^m = X_1^2 \varepsilon_{11}^* v_{11}^{*m} + 2X_1 X_2 \varepsilon_{12}^* v_{12}^{*m} + X_2^2 \varepsilon_{22}^{*m}; \quad m = 2, 4 \quad (6.49a)$$

Eq. (6.49a) has six parameters, four of which are accessible from the *PVT* measurements of neat components (*e.g.*, polymer-1 and polymer-2), thus the two cross-interaction parameters, ε_{12}^* and v_{12}^* , can be determined, indicating attractive or repulsive cross-interactions. It is noteworthy that strong attractive energetic interactions usually lead to smaller value of the volumetric interaction parameter. For the ease of computations, Eq. (6.49a) was rearranged into:

$$\begin{aligned} \langle v^* \rangle^2 &= \frac{\Xi_4}{\Xi_2} \times v_{11}^{*2}; \quad \text{and} \quad \langle \varepsilon^* \rangle = \frac{\Xi_2}{\Xi_4} \times \varepsilon_{11}^* \\ \Xi_2 &\equiv X_1^2 + 2X_1 X_2 e_{12} v_{12}^2 + X_2^2 e_{22} v_{22}^2 = \left(\frac{\langle v^* \rangle}{v_{11}^*} \right)^2 \left(\frac{\langle \varepsilon^* \rangle}{\varepsilon_{11}^*} \right) \\ \Xi_4 &\equiv X_1^2 + 2X_1 X_2 e_{12} v_{12}^4 + X_2^2 e_{22} v_{22}^4 = \left(\frac{\langle v^* \rangle}{v_{11}^*} \right)^4 \left(\frac{\langle \varepsilon^* \rangle}{\varepsilon_{11}^*} \right) \end{aligned} \quad (6.49b)$$

where: $e_{12} \equiv \varepsilon_{12}^* / \varepsilon_{11}^*$; $e_{22} \equiv \varepsilon_{22}^* / \varepsilon_{11}^*$; $v_{12} \equiv v_{12}^* / v_{11}^*$; $v_{22} \equiv v_{22}^* / v_{11}^*$.

The hole fraction, h , computed from the *PVT* data, was found to correlate with the static (thermodynamic equilibrium) and dynamic properties, *e.g.*, flow of polymers [Utracki, 1986] as well as their blends, foamed compositions [Utracki and Simha, 2001] composites and nanocomposites (*viz.* Chapter 15 of this book).

6.4.2 Gas solubility in polymers

Given reliable *PVT* description of polymer melts and their mixtures [Xie *et al.*, 1992], the equilibrium behavior of a polymer with a gas phase was analyzed. During the last 20 years, the studies of gas-polymer sorption enjoyed great advances on two fronts:

- 1) Attempts of circumventing an apparent upper bound on gas-permeability and selectivity through polymeric membranes [Robeson, 1991].
- 2) The need for understanding polymer-gas physics of foaming that would ease replacement of banned or regulated halogenated blowing agents by benign gases, *e.g.*, N₂ or CO₂.

Xie and Simha [1997] extended the S-S equations for binary mixtures for predicting the sorption of gases in equilibrium with PS, assuming equality of the chemical potentials of the overlying gas phase (μ_{11}) and the polymer-gas mixture (μ_{12}). For the vapor phase the difference in chemical potential of a gas from its ideal-gas law chemical potential is:

$$\Delta\mu = \int_V^\infty (P - RT/V)dV + (PV - RT) \quad (6.50)$$

Equation (6.50) has been applied to eos of 1,1,1,2-tetrafluoroethane (HFC 134a) [Simha and Xie, 1998] and CO₂ [Simha and Moulinié, 2000; Li *et al.*, 2006a,b] for calculating their solubility in PS. For a gas molecule of molar mass M and 3-degrees of freedom:

$$\mu_{11} = RT \ln \left\{ \frac{P(N_a h)^3}{kT(2\pi MRT)^{3/2}} \right\} + \Delta\mu \quad (6.51)$$

The gas-polymer mixture was modeled as a liquid mixture, whereby the gas behaved as a solute in the polymer. Accordingly, the Gibbs free energy of the mixing was expressed using equations derived for mixtures [Jain and Simha, 1980]:

$$\begin{aligned} G_m / RT = & x_1 \ln x_1 + (1 - x_1) \ln(1 - x_1) + \ln(y/s) \\ & + s(1 - y) \ln(1 - y) / y + (s - 1) \ln[e/(z - 1)] - c[\ln(v^* / N_a) \\ & \times (1 - \eta)^3 / Q] + cyQ^2(1.011Q^2 - 2.409) / 2\tilde{T} \\ & - \frac{3}{2}c_1x_1 \ln[2\pi M_1 RT / (N_a h)^2] - \frac{3}{2}c_2(1 - x_1) \ln[2\pi M_2 RT / (N_a h)^2] \\ & + (c / Ms)[(1 - \eta)^{-1} + 2yQ^2(1.011Q^2 - 1.2045) / \tilde{T} \end{aligned} \quad (6.52)$$

For a high molecular weight polymer, $\langle s \rangle \langle M \rangle = x_1 s_1 M_1 + (1 - x_1) s_2 M_2$, whereby the modeled polymer segment size was tailored to the molecular weight of the solute. The explicit expression for the chemical potential of the condensed phase:

$$\mu_2 = G_m + (1 - x_1) \partial G_m / \partial x_1 \quad (6.53)$$

was reported by Nies *et al.* [1990].

Theoretical sorption calculations of HFC 134a in molten PS gave excellent agreement with gravimetrically measured solubility [Wong *et al.*, 1998]. The development of magnetic suspension balances capable of accurately measuring gas solubility at high temperature and pressure has yielded valuable data for further studying the validity of mixing assumptions from S-S theory. When deriving eos for the mixture, the mixing rules for the volume and maximum attraction energy of the mixture were determined as averages computed from those of the neat components [Jain and Simha, 1984]. The L-J interaction parameters of hetero-contacts were approximated by averages; the attractive energy by the geometric average (Berthelot's rule):

$$\varepsilon_{12}^* = \delta_\varepsilon (\varepsilon_{11}^* \varepsilon_{22}^*)^{1/2} \quad (6.54)$$

while the repulsion volume by the arithmetic average:

$$v_{12}^* = \delta_v (v_{11}^{*1/3} + v_{22}^{*1/3})^3 / 8 \quad (6.55)$$

Equations (6.54) and (6.55) incorporate adjustable parameters δ_ε and δ_v , with values closed to unity; Simha and Moulinié [2000] discussed their effects on the solubility for CO₂-PS. Conceptually, stronger attractive forces increase solubility, while increased repulsive volume reduces it. These parameters might be determined from reliable experimental data. Table 6.3 lists the values derived from CO₂ solubility in PS or polylactic acid (PLA):

Table 6.3. Solubility in PS and PLA.

System	δ_e	δ_v	References
CO ₂ – PLA	1.0515	0.9945	Li <i>et al.</i> , 2006
N ₂ -PLA	1.1722	1.0414	Li <i>et al.</i> , 2006
CO ₂ – PS	1.0650	1.0650	Simha and Moulinié, 2000

The values of δ_e and δ_v were computed using Marquardt-Levenberg minimization of the differences between calculated and measured values. The values ≤ 1 indicate decreased solubility. For CO₂ the solubility curves in PS appear to require greater compensation for repulsive and attractive forces than that in PLA. Furthermore, there appears to be greater necessity to reconcile theoretical predictions from N₂-PLA than from CO₂-PLA. Further model studies coupled with experimental data would help better understanding the performance of these mixtures and the role of the repulsive and attractive contributions.

6.4.3 Polymer blends

In the technology of polymer blends, the magnitude of interactions between segment pairs is essential for understanding the phase behavior [Utracki, 1989, 1998]. Because of the small thermal effects and high viscosity, the blends analysis via *PVT* measurements offers the unique possibility for examining interactions in miscible mixtures.

Figure 6.3. The average Lennard-Jones scaling parameters for PPE/PS blend in the full range of concentration; re-computed from [Utracki and Simha, 2001].

The *PVT* data of PPE, PS and their blends [Zoller and Hoehn, 1982; Jain *et al.*, 1982; Zoller and Walsh, 1995] were analyzed using Eqs. (6.35) and (6.49); the standard deviation ranged from 0.0009 to 0.0016 and the correlation coefficient squared was $r^2 \geq 0.999997$ [Utracki and Simha, 2001]. The compositional variation of the L-J average interaction parameters is displayed in Figure 6.3, and values of the $\varepsilon_{ij}^*, v_{ij}^*$ parameters are listed in Table 6.4. The parameters $\varepsilon_{ii}^*, v_{ii}^*$ of neat polymers were measured, while those of the hetero-contacts, $\varepsilon_{12}^*, v_{12}^*$, were calculated from Eq. (6.49), assuming that the intrinsic interactions of each neat polymer remain unaffected by the presence of the other. The listed values suggest that energetic interactions between PPE and PS are stronger than that within each polymer, and consequently the repulsive volume is smaller. Thus, mainly the enthalpic effects control the miscibility between PS and PPE.

Table 6.4. The Lennard-Jones scaling parameters for PPE, PS and their blends

Polymer	ε_{ii}^* (kJ/mol)	v_{ii}^* (mL/mol)	ε_{12}^* (kJ/mol)	v_{12}^* (mL/mol)
PPE	30.1	35.6	--	--
PS	33.6	42.3	--	--
PPE/PS blend	--	--	36.5 ± 2.5	31.5 ± 2.0

6.4.4 Polymeric composites

The S-S eos extended to binary systems, Eqs. (6.35) and (6.49), have been used for the interpretation of properties of particulate-filled polymeric composites [Simha *et al.*, 1984]. The reduced bulk modulus, $\tilde{K}$, was derived by differentiation of Eq. (6.35), and that of the thermal expansion coefficient at ambient pressure by differentiation of Eq. (6.23a):

$$\begin{aligned}
 \tilde{K} = \tilde{\kappa}^{-1} &\equiv -\left(\partial \tilde{P} / \partial \ln \tilde{V}\right)_{\tilde{T}} ; \quad \tilde{\alpha} \equiv \left(\partial \ln \tilde{V} / \partial \tilde{T}\right)_{\tilde{P}} \\
 \therefore \tilde{K} \tilde{V} / \tilde{T} &= \tilde{P} \tilde{V} / \tilde{T} + (\eta/3)(1-\eta)^{-2} + 4y(2AQ^4 - BQ^2)/\tilde{T} - \\
 &\quad \left\{ (2\eta/3)(1-\eta)^{-2} - 2y(3AQ^4 - BQ^2)/\tilde{T} \right\}^2 \times \\
 &\quad \left\{ (4\eta/3)(1-\eta)^{-2} - y(9AQ^4 - 2BQ^2)/(2\tilde{T}) + (s/c) \left[(1-y)^{-1} + (1/y) \ln(1-y) \right] \right\}^{-1} \\
 \therefore \tilde{\alpha} &= (3/2)b\sqrt{T/T^*}^3
 \end{aligned} \tag{6.56}$$

The two expressions are implicitly valid for equilibrium liquids, but might be extended to non-equilibrium glasses (see Part 6.5) and semi-crystalline polymers. For rigid reinforcing particles $3c/s \rightarrow 0$, while for the flexible matrix molecules $3c/s = 1$. Theoretically, the segment size for the two components is about equal, thus the number of segments in filler particles is *ca.* 12-orders of magnitude greater than that in macromolecules.

Equation (6.56) was used for determining the effects on bulk modulus of the relative polymer/filler interactions, $e_r \equiv \varepsilon_{12}^* / \varepsilon_{11}^*$, and the filler volume fraction, ϕ_2 . The specific bulk modulus is:

$$K_{sp} / \phi_2 = [K(\phi_2) - K(0)] / [\phi_2 K(0)] = [K](1 + a_1 \phi_2 + \dots) \quad (6.57)$$

Interestingly, at low values of $e_r \approx 1$, the intrinsic bulk modulus $[K] = 1.0$ and $a_1 \approx 10$, both agreeing with expectations. The relative flexibility parameter, $f = (c_2/s_2)/c_1/s_1$, ranged from 0 (rigid filler particles) to 1 (flexible molecules). As expected, softening the particles reduced the bulk modulus, but the effect at $e_r = 1.2$ was small. Differences between the computed and measured α -coefficients occurred at high filler loading. They most likely originated in filler aggregation, hence in changes of $e_r = e_r(\phi)$.

In the following papers [Simha *et al.*, 1986; Papazoglou *et al.*, 1989; Simha *et al.*, 1989] the above model was compared with one based on the theory of elastic continua. Even though the two theories started from different perspectives, *viz.* elasticity *vs.* statistical thermodynamics, it was tempting to establish relationships between the model parameters and correlate microscopic quantities. For the bulk modulus, a correspondence between the two theories at infinite dilution was noted, although the comparison was complicated by the presence of the interlayer, which required a reformulation of the equation of state properties for the interphase. The two theories lead to identical limiting values for the reduced α , but the concentration dependencies were different. Since in the S-S theory both α and K are derived from eos, the same $\varepsilon_{ij}^*, v_{ij}^*$ parameters determine both functions and suggest inter-relation; *viz.* Eqs. (6.11), (6.35), and (6.45)-(6.49). The concentration dependences of α and K , calculated from either theory, agreed well with experiments on polyurethane and epoxy composites. The eos-model is always capable of

predicting α from experimental values of K , whereas the other theory requires knowledge of relations between α and K of the constituents [Simha *et al.*, 1989].

6.4.5 Polymeric nanocomposites (PNC)

Polymeric nanocomposites (PNC) are materials composed of a macromolecular matrix and dispersed in it solid particles having at least one dimension within a low nanometer range, ≤ 2 nm. Their *PVT* behavior very much resembles that of a matrix, and the theoretical models describe the behavior with similar precision as that of neat polymer [Utracki, 2007a, 2008a]. The measurements are time consuming since addition of 1-5-wt% clay (or 0.4 to 2-vol%) has a small effect on V , and thus high reliability and repeatability of data is critical. The most common PNC today are those comprising dispersed clay platelets, known as clay-containing polymeric nanocomposites, or CPNC [Utracki, 2004].

Evidently, the most pertinent question is on the effect of nano-particles on the structure and physical properties. The experiments show that addition of clay affects the mechanical properties, gas permeability, flammability, biodegradability, *etc.* In well-prepared CPNC, the effects are astonishingly large, *e.g.*, the modulus may double after incorporation of *ca.* 1.4-wt% or 0.6-vol% of clay [Utracki, 2008b]. The key for achieving the maximum enhancement of performance is the understanding of the fundamental mechanism in CPNC. In this context, the *PVT* measurements and their interpretation via S-S eos have proven to be particularly useful. Since Chapter 15 is dedicated to this topic, here only brief summary is provided.

The *PVT* data fitted to Eq. (6.35) give two sets of information: (1) the free volume content, $h = h(P, T)$, and (2) the reducing parameters; $\langle P^* \rangle$, $\langle V^* \rangle$ and $\langle T^* \rangle$, from which the L-J interaction parameters might be computed [Simha *et al.*, 2001; Utracki *et al.*, 2003; Utracki, 2007b]. In these studies a commercial CPNC with *ca.* 2-wt% (0.64-vol%) of organoclay, well dispersed (exfoliated) in the poly- ϵ -caprolactam (PA-6) matrix was used. The specific volume and hole fraction h are displayed in Figure 6.4 as the ratios $V(\text{PA})/V(\text{PNC})$ and $h(\text{PA})/h(\text{PNC})$ within the same range of independent variables ($T = 500 - 600$ K and $P = 0.1 - 190$ MPa). Reduction of the specific volume by *ca.* 1% was expected from the volume additivity, but the simultaneous loss of free volume by *ca.* 15% was not. Empirically, as shown in Figure 6.5, at

constant clay content of 2-wt% the h -loss, $\Delta h(\%) = 100[1 - h(\text{PNC})/h(\text{matrix})]$, correlates with the interlayer spacing, d_{001} [Tanoue *et al.*, 2004; Utracki and Simha, 2004b].

The h -loss, Δh , initially linearly increases with the clay content, but at higher concentrations, it goes through a local a maximum. It is noteworthy that while the magnitude of Δh depends on the system (*i.e.*, on d_{001} , *viz.* PS and PA systems in Figure 6.5) the concentration for the maximum reduction of free volume is about the same, $w_{\max} \approx 3.6 \pm 0.1$ wt% organoclay, or *ca.* 1 vol% of inorganic clay. Thus, the Δh level correlates with the ability of clay to adsorb and solidify macromolecules – initially the total available surface linearly increases with concentration, but at higher loading full exfoliation is not feasible and decreases of the area due to collapsing of interlayer spacing dominates the behavior.

Figure 6.4. Relative V and h vs. T for $P = 0.1$ to 190 MPa for commercial PA-6 based CPNC from Ube [Simha *et al.*, 2001].

Figure 6.5. Loss of free volume by addition of 2-wt% organoclay vs. interlayer spacing [Tanoue *et al.*, 2004].

In the binary systems the characteristic reducing parameters $\langle P^* \rangle$, $\langle V^* \rangle$, $\langle T^* \rangle$ and calculated from these interaction parameters, $\langle \varepsilon^* \rangle$ and $\langle v^* \rangle$, are bulk-averaged. Owing to the discussed above changes of the solidification extend with concentration, the direct computation of the individual interaction parameters, ε_{ij}^* , v_{ij}^* , from Eqs. (6.48) and (6.49) is not possible – one needs a model how the CPNC structure changes with concentration.

The “hairy clay platelets” (HCP) model was formulated considering the reduction of molecular mobility near a crystalline surface [Utracki and Lyngaae-Jørgensen, 2002; Fleer *et al.*, 1993; Hentschke, 1997]. The organic compounds form a solid layer on the clay [Cosgrove *et al.*, 1987, 1991]. The surface force analyzer (SFA) showed that there are two layers of reduced mobility. The first solid layer is ca 2-9 nm thick in the orthogonal z -direction from the clay surface, while the second layer extends to a distance $z_c = 60$ to 120 nm; the full segmental mobility was observed only above the latter limit [Israelachvili *et al.*, 1984; Horn and Israelachvili, 1988; Luengo *et al.*, 1997]. The HCP model implies that in diluted systems ($\phi < 0.005$, where the clay platelets are more than 200 nm apart) individual HCP are dispersed in a polymeric matrix and the values of the interaction parameters are constant. As the concentration increases, the domains of reduced mobility around HCP overlap, macromolecules with bulk properties disappear, and the interactions depend on composition. Incorporation of the HCP model into Eqs. (6.48), (6.49), (6.54) and (6.55) lead to the concentration-dependent variable matrix interaction parameters, $\varepsilon_{II}^* = \varepsilon_{II}^*(X_I)$ and $v_{II}^* = v_{II}^*(X_I)$, with values consistent with those obtained from homopolymers [Utracki, 2004]; see also Chapter 15 of this book.

6.5 Extension to non-equilibrium states

Correlation between liquid behavior at thermodynamic equilibrium and that in flow follows from the mean-field approach, which assumes that liquids are structure-less, and that the dynamic behavior can be considered a semi-equilibrium state. Evidently, this approach is unable to explain kinetic phenomena.

The S-S lattice-hole mean field theory does not consider polymeric chain structure, but its effects are reflected in the values of the characteristic reducing parameters, P^* , T^* , V^* , and the L-J scaling parameters. Characteristically, the PVT data do not indicate the secondary transformation temperatures at *ca.* $0.8T_g$ and $1.2T_g$, detectable in derivative properties (see Figures 6.1 and 6.2). By contrast, all flow models, *e.g.*, reptation, cell structures, hole jumping, implicitly postulate that such configurational or conformational changes affect liquid dynamic behavior.

6.5.1 Viscosity and viscoelasticity

Batchinski observed that zero-shear viscosity (η_0) of low molecular weight liquids at different T and P changes with the density, ρ : $\eta_0 \propto \rho$ [Batchinski, 1913]. Later Doolittle correlated $\ln \eta_0$ with redefined free volume, also calculated from density [Doolittle, 1951a,b, 1952, 1954; Doolittle and Doolittle, 1957]:

$$\ln \eta_0 = a_o - a_1 / f_D; \quad f_D \equiv V_f / V_o = f / (1 - f) = (1 / b\rho) - 1 \quad (6.58)$$

Several authors examined validity of this empirical dependence replacing the empirical f_D with free volume or hole fraction, *e.g.*, calculated from PVT data by means of Eq. (6.35) [Utracki, 1974, 1983a, 1983b, 1985, 1986; Utracki and Simha, 1981b,c; Utracki and Ghijssels, 1987; Kadijk and van den Brule, 1994; Sedlacek *et al.*, 2004, 2005]:

$$\ln \eta = a_o + a_1 Y_s; \quad Y_s = 1 / (h + a_2) \quad (6.59)$$

where η is taken as either the zero-shear viscosity, η_0 , or viscosity at constant stress, $\eta = \eta(\sigma_{12} = \text{const})$. Eqs. (6.58) and (6.59) predict that η is a function of T and P only through $h(T, P)$. For n -paraffins, their mixtures, as well as silicone oils and polymers good superposition was found in wide ranges of variables (*e.g.*, $T = 20\text{-}204^\circ\text{C}$ and $P = 0.1\text{-}500$ MPa), with constant values of the parameters: $a_1 = 0.79$ and $a_2 = 0.07$. The parameter a_2 only linearizes the dependence. However, for polymers a_1 depends on the molecular weight distribution, MWD, and the melt structure changes at a secondary transition temperature $T_T > T_g$.

Superimposition of the viscosity data below and above, $T_T \approx T_c \approx T_B \approx T_{LL}$ (see Chapter 15), requires different characteristic parameters in Eq. (6.59), and/or different characteristic pressure reducing parameter for flow (P_R^*) than that for the PVT , *viz.* $P_R^* = \xi P^*$, where the factor ξ depends on the polymer. In a recent publication η and PVT , data were determined within the same range of T and P (see Figure 6.6). If the lack of superposition of $\log \eta$ vs. $1/h$ data for molten polymers originates in variable structures, it is reasonable to expect that as T increases the thermal motion randomize the distribution of lattice elements, improving superposition of data.

Indeed, the $\xi \equiv P_R^*/P^* = 6.81 - 3.82T/T_g$ was found with $r = 0.997$; predicting that $\xi = 1$ at $T \approx 1.52T_g$ for the glassy polymers. [Utracki and Sedlacek, 2007].

Figure 6.6. Plot of $\ln \eta$ vs. Y_s for the eight polymers; see Eq. (6.59). The parameter ξ ranged from 1 for high- T PP, to 2.1 for PMMA [Utracki and Sedlacek, 2007].

Boyer [1977, 1980a, 1980b, 1985, 1987] reported the existence of the “liquid-liquid transition temperature” $T_{LL}/T_g = 1.20 \pm 0.05$. Molecular modeling and vibrational spectra measurements established several relaxational modes at $1 < T/T_g < 1.6$, which affect the T and P dependencies of liquid viscosity or relaxation time [Jäckle, 1986; Kanaya *et al.*, 1999; Kanaya and Kaji, 2001; Binder *et al.*, 2003; Bicerano, 2003]. The mode-coupling theory (MCT) considers liquid as an assembly of particles enclosed in cages formed by their neighbors; the α -relaxation controls the behavior at $T < T_c$, while at $T > T_c$ molecular vibrations dominate the liquid behavior [Casalini and Roland, 2005; Roland *et al.*, 2006]. The crossover temperature, T_c , of these two mechanisms: $T_c/T_g = 1.15$ to 1.35 , is close to Boyer’s T_{LL} [Kisliuk *et al.*, 2000]. Furthermore, the polymer dynamics at temperatures below T_c is complicated by the presence of other processes that originates is backbone chain vibrations or side group motion [Ngai, 2000, 2003]. Thus, in macromolecular liquids at $T > T_g$ there are several relaxation processes, some different from those of simple, low molecular weight liquids. The difference diminishes as the temperature increases. Boyer also reported transition at still higher temperature, $T_{Lp} \approx T_{LL} + 50 \approx 1.4T_g$, which he named “the intramolecular relaxation transition” that separates structured polymer melt from the “true liquids” [Boyer, 1977, 1980a, 1980b, 1985, 1987].

The polymer dynamics involves several relaxation processes, some of which start within the vitreous region and cross to high temperature melts. For example, the fast relaxations of the backbone chain or side groups start near the Vogel-Fulcher-Tammann-Hesse (VFTH) temperature and extend to $T > T_c$. The linearized VFTH expression:

$$\begin{aligned} \log \eta_0(T) &= A + B / (T - T_0) \\ \text{linearized: } [d \log \eta / d(1/T)]^{-1/2} &= B^{-1/2} (1 - T_0/T) \end{aligned} \quad (6.60)$$

defines two transition temperatures, $T_A > T_B$, the former defining the lower limit of the Arrhenius-type dependence, whereas the latter indicating a crossover of two VFTH dependencies at $T_B \approx T_c$ [Stickel *et al.*, 1995, 1996; Ngai, 2000 and 2003].

Thus, considering that several relaxation processes exist at $T > T_g$, attempts to describe the flow properties with a single equation may fail. The relation between the equilibrium thermodynamic quantity such as hole or free volume fraction might be correlated with the dynamic behavior of polymer melts only within a range of T and P where the structure remains constant. This conclusion is equally valid for Eq. (6.59) as for the empirical relations proposed by Batchinski or by Doolittle [Utracki and Sedlacek, 2007]. It is noteworthy that the latter relation is the cornerstone of the viscoelastic behavior, the time-temperature superposition principle (t - T) [Ferry, 1980]. The t - T shift factor has been interpreted following Doolittle's free volume arguments, cast in the form of the WLF equation [Williams *et al.*, 1955]. However, the following statement by the authors should be noted: *"Above $T_s + 50$ (or $T_g + 100$) the equation fails because different systems show specific properties which are no longer dominated by the non-specific behavior associated with supercooling and vitrification. ... It is only in supercooled liquids, within 100° above the point of vitrification, that an abnormally high temperature – independent of molecular structure – overwhelms such specific differences and makes possible our universal function."* Accordingly, the WLF equation is valid at $T_g < T < T_g + 100^\circ\text{C}$, while good correlation is often observed in narrower span of T (e.g., 60 - 80°C above T_g). Since the rotational diffusion coefficient is inversely proportional to viscosity, similar limitations might be expected [Debenedetti and Stillinger, 2001]. Several books, e.g., [Utracki, 1989, 2002, 2004] and Chapter 18 in this volume discuss the influence of the free volume on flow behavior.

6.5.2 Glassy state and physical aging.

The glass transition is a process in which molten polymer is transformed into glass, or vice versa. The glass transition temperature marks freezing-unfreezing temperature of micro-Brownian motion involving 20 to 50 carbon atoms at $T_g \approx (2/3)T_m$. In vitrified polymers, there is a secondary transition at $T_\beta \approx (0.75 \pm 0.05) \times T_g$. Several reviews describe the experimental and mathematical models of vitrification, glass transition and glass properties of the glass-formers [Ngai, 2000, 2003; Debenedetti and Stillinger, 2001; Ediger *et al.*, 1996; Di Marzio and Yang, 1997; Drozdov, 1999; Ediger, 2000].

Formally, liquids are supercooled below the melting point, $T_m \approx 1.5T_g$. The MCT theory assumes a cell-like structure, in which the main relaxation process is segmental; the particles vibrate at high frequency, either inside their cell-like domains or jump between them. As T decreases below T_c , the structural relaxation mode takes over. The latter mode persists to temperatures well below T_g , where the fast and the characteristic for polymers elementary relaxations are present. At $T < T_g$ immobile clusters, and mobile defects dominate the material behavior [Kanaya and Kaji, 2001; Binder *et al.*, 2003].

Angell classified liquids at $T \geq T_g$ as strong (which follow the Arrhenius temperature dependence, *e.g.*, SiO_2) and fragile [Angell, 1985, 1995; Ito *et al.*, 1999; Böhmer *et al.*, 1993]; polymers belong to the latter category. Two mechanisms may produce such behavior: either the glass-former structure is heterogeneous with domains showing different exponential relaxations, or homogeneous where the domain relaxations are inherently non-exponential [Richert, 1994; Hansen *et al.*, 1997; Bauer *et al.*, 2000]. There is evidence that the former possibility is correct [Ediger *et al.*, 1996; Ediger, 2000; Sillescu, 1999]. The heterogeneity of structure has been identified by the presence of domains 2 to 10 nm diameter with dynamics of neighboring blobs differing by 1 to 5 decades and having different temperature dependencies.

Upon cooling, the glass forming liquids follows the α -process responsible for increasing the viscosity by *ca.* 10 orders of magnitude and formation vitreous phase. As evidenced by the universality of the Boson peak at $T = 5$ to 20 K, the heterogeneous structure observed in supercooled liquids remains – the blobs accommodate several mer units. At the same time, the vitreous structure depends on the vitrification process, *e.g.*, on the cooling or compressing rate, q ,

on the P during the cooling, or T during the compressing, *etc.* Each glass-former has a spectrum of states with different structures and the physical aging kinetics (PAK). [Utracki, 2007a; Cowie *et al.*, 2002]. The structure determines the rate and magnitude of PAK at $T_\beta/T_g \leq T/T_g \leq 1$ [Struik, 1978]. The rate of physical aging is zero at the limiting temperatures, reaching a local maximum halfway in between. For example, for polycarbonate (PC) $T_\beta \approx 140$, $T_g = 420$ K and PAK shows a broad maximum at *ca.* 280 K [Struik, 1978]. However, within this range of temperatures the neutron scattering and dielectric spectroscopy shows that molecular motions with the characteristic time of 10^{-10} to 10^{-9} s systematically increase from zero at T_β to a high plateau at T_g . The vibrations of different molecular groups are coupled, *e.g.*, rotation of the phenyl rings is related to motion of the carbonate and methyl groups [Arrese-Igor *et al.*, 2006].

Considering the diversity of the glass-formers, it is understandable that the glass transition theories remain controversial, unable to accommodate all the observed aspects [Ngai, 2007]. During the last decade or so the focus has been on the kinetics – the discovery of the different dynamic processes across the observable transition temperatures is highly illuminating as far as physics and philosophy are concerned. However, thermodynamics is the cornerstone of material science and its laws determine what may take place. The thermodynamics consider the glass transition to be rate-affected second order, pseudo-equilibrium transition; with time, its free energy tends toward a minimum. The process that might be described using explicitly an extensive quantity, $Q = Q(P, T, P', q)$, (where q is the cooling rate at the pressure P') [Simha, 1977], or by an additional entropy term related to slow configurational processes that vanish at equilibrium [Nieuwenhuizen, 2000].

According to Eq. (6.34), the S-S eos was derived for thermodynamic equilibrium conditions. In the vitreous state, the configurational thermodynamics depends on P , T , the way glass was prepared, and on time, thus the occupied volume fraction: $y \equiv 1 - h = y(P, T, t_a)$, where t_a is the annealing time. Accordingly, McKinney and Simha replaced the standard definition of pressure in Eq. (6.34) by the general function of $\tilde{T}$, $\tilde{V}$ and y [McKinney and Simha, 1974, 1976]:

$$-\tilde{P} = \left(\partial \tilde{F} / \partial \tilde{V} \right)_{\tilde{T}, y} + \left(\partial \tilde{F} / \partial y \right)_{\tilde{T}, \tilde{V}} \left(\partial y / \partial \tilde{V} \right)_{\tilde{T}} \quad (6.61)$$

The authors computed the derivatives by iterative numerical method. Alternatively, the *PVT* data were analyzed using only the second relation in Eq. (6.35) for calculating the free volume from the experimental *PVT* data and the characteristic reducing parameters, P^* , T^* , V^* (determined in the melt). The difference between the results calculated following the latter *simplified* procedure and the exact numerical solutions was $\leq 10\%$. The analysis opened a way for the use of the S-S theory for analyzing the time-dependent properties of polymer glasses.

Curro *et al.* [1981] followed a similar procedure in studies of the aging kinetics of polymethyl methacrylate (PMMA). For predicting the shift factors of aging experiments at 23°C, the authors computed from *PVT* values of h and then substituted these into Doolittle Eq. (6.58). The resulting prediction agreed with the experimental values, contrasting with inadequacy of the WLF relation. Next, the aging was modeled as a diffusion of free volume [Curro *et al.*, 1982].

Chapter 15 discusses the use of the S-S eos to the physical aging of PS-based clay-containing polymeric nanocomposites. The presence of $w \geq 3.6$ wt% clay resulted in freezing large free volume fraction, $FF > 1$.

In a series of publications started in 1978 Robertson [1978, 1979] developed stochastic interpretation of the relaxation processes in glassy polymers near T_g . The author assumed that relaxation proceeds by conformational changes with rates controlled by the local free volume. Initially, he considered two sources of free volume – an average, associated with free space and described by WLF, and the one formed by coordinated molecular motions; the thermal free volume fluctuations he incorporated as well. The results qualitatively agreed with experimental findings. At the next step, the stochastic method was integrated with the S-S theory [Robertson *et al.*, 1984, 1988; Robertson, 1992]. Simulation well reproduced maxima in the volume vs. time curves observed before equilibrium. Drozdov [1999] discussed some drawbacks of the model. More recently, the stochastic treatment of volume relaxation was cast in form of a Schrödinger-type equation [Simha and Robertson, 2006]. This step on the one hand facilitates numerical solution, and on the other, it readily accommodates diverse conditions such as, *e.g.*, physical aging under stress (Chapter 4 of this book provides more details).

The S-S theory has been also used for the computation of the thermal density fluctuation in the molten and glassy state [Balik *et al.*, 1982]:

$$\langle \delta \rho^2 \rangle = k_B T \rho^2 \kappa_l / V \quad (6.62)$$

where ρ is number density and κ_l the isothermal liquid compressibility. For the molten state, the theory fully predicted the behavior, but for the glass, the calculations involved numerical solution of Eq. (6.61), with the results cast as isobaric polynomials. The computations showed relatively good agreement with the Fisher-Wendoff approximation of Eq. (6.62) after replacing κ_l by its value at T_g .

6.6 Summary, conclusions and outlook

The chapter contains three parts: (1) evolution of the eos for diverse fluids, (2) formulation of the S-S hole-cell theory for the configurational free energy in single- and multi-component systems, and (3) application of the S-S eos to polymeric systems at thermodynamic equilibria and under non-equilibrium conditions.

During the last four decades, the theory has been applied to a diversity of systems, polymeric and non-polymeric in nature, providing description, interpretation and prediction of their behavior. The greatest benefits it brought to multi-component polymeric systems providing direct information on the magnitude of interactions and the degree of dispersion, hence on the structure. The explicit incorporation of the free volume parameter, $h = h(P, T)$, is particularly valuable for the dynamic behavior in the molten and glassy state. Given the success of the theory in offering guidance for polymer processing, *e.g.*, for extrusion foaming, there will be continued industrial interest in examining aging of polymer-gas mixtures (*e.g.*, aged foams).

During the last few years, the attention shifted toward the glassy state where the performance depends on the extent of “freezing” the free volume parameter. The physical aging of vitreous multi-component systems was successfully interpreted by means of the S-S eos. These aspects, along with applications of the S-S eos to surface tension, and to PALS are discussed in other Chapters in this book.

6.7 Abbreviations

BWR	Benedict-Webb-Rubin equation
$\tilde{C}\tilde{E}\tilde{D}$	Reduced cohesive energy density
CPNC	Clay-containing polymeric nanocomposites
CSP	Corresponding states principle
D-W	Dee and Walsh
eos	Equation of state
FOV	Flory, Orwoll, and Vrij
HCP	Hairy clay platelets
HFC 134a	1,1,1,2-tetrafluoroethane
H-H	Hartmann and Haque
ISM	Ihm, Song and Mason
L-J	Lennard-Jones
MC	Monte Carlo
MCM	Modified cell model (by Dee and Walsh)
MCT	Mode-coupling theory
MD	Molecular dynamics
MSS	Modified S-S eos
NMR	Nuclear magnetic resonance
PA-6	Poly- ϵ -caprolactam
PAK	Physical aging kinetics (at $T_\beta \leq T \leq T_g$)
PALS	Positron annihilation lifetime spectroscopy
PLA	Poly(lactic acid)
PMMA	Polymethyl methacrylate
PNC	Polymeric nanocomposites
PPE	Poly(2,6-dimethyl 1,4-phenylene ether)
PS	Polystyrene
PTM	Prigogine, Trappeniers and Mathot
PVT	Pressure-volume-temperature measurements or surface
SANS	Small angle neutron scattering
SFA	Surface force analyzer
S-G	Spencer-Gilmore
S-L	Sanchez-Lacombe
S-S	Simha-Somcynsky
SWP	Square-well potential approximation
VDW	Van der Waals
VFTH	Vogel-Fulcher-Tammann-Hesse
WLF	William-Landel-Ferry
XRD	X-ray diffraction

6.8 Symbols

6.8.1 Roman

$3c$	Number of the external degrees of freedom.
$a = a(T)$	van der Waals measure of interactions
a_n	ISM parameter (VDW analogue)
A, B	PTM coefficients $A = 1.011$ and $B = 1.2045$ for the face-centered cubic lattice with the coordination number $z = 12$
A_2	Second virial coefficient
$B(T)$	Bulk modulus
$b, b = b(T, V)$	Clausius <i>covolume</i> , or van der Waals “excluded volume”
b_n	ISM parameter (VDW analogue)
B_o	Bulk modulus isothermal value evaluated at a reference pressure, P_o .
C	Tait equation constant ≈ 0.0894
C_d	Coefficient of determination
E_o	L-J potential
F	Helmholtz free energy
$f = (c_2/s_2)/c_1/s_1$	Relative flexibility parameter
$f = V_f/V$	Free volume fraction
g	Combinatorial factor
G_m	Gibbs free energy of the mixing
$h = 1 - y$	hole fraction
$h = h(T, P)$	S-S free volume content
k	Boltzmann’s constant
$[K]$	Intrinsic value of the bulk modulus
K	Reduced compressibility; $P^*V^*/RT^* = 3/8$ to 0.272
l	Segment length
M_n, M_w	Number, weight averaged molecular weights
$M_s = M_n/s$	Segmental molecular weight (M_n is the number-averaged molecular weight)
n	Number of molecules in volume V
$p_i, \tilde{p}_i$	Internal pressure and its reduced value
P	pressure
$\tilde{P}$	Reduced Pressure (P/P^*)
P^*, T^*, V^*	Pressure, Temperature, volume reducing parameters, respectively
$P_R^* = \xi P^*$	Characteristic pressure reducing parameter in flow
P_c, V_c and T_c	Critical point coordinates
R	Gas constant
r^2	Correlation coefficient squared
S, S_o	Number of external contacts for segment (-mer) and hole
s	Number of statistical segments ($s = M_n/M_s$)
T	temperature
T_c	Cross-over or secondary transition temperature: $T_c/T_g = 1.25 \pm 0.10$
T_d	Degradation temperature
T_g	Glass transition temperature; $T_g \approx (2/3)T_m$

T_{LL}	“Liquid-liquid transition temperature” $T_{LL}/T_g = 1.20 \pm 0.05$
T_{Lp}	Boyer higher melt transition temperature, $T_{Lp} \approx T_{LL} + 50 \approx (1.35 \pm 0.1) \times T_g$
T_m	Melting temperature, $T_m \approx 1.5T_g$,
T_β	Secondary, sub-glass transition temperature: $T_\beta \approx (0.75 \pm 0.05) \times T_g$
$\tilde{T}$	Reduced temperature (T/T^*)
U	Internal energy of the system
$\tilde{V}$	Reduced volume (V/V^*)
$\tilde{V}_o$	Reduced volume ($V(0, T)/V^*$) at $P = 0$
V	Specific volume
V_f	Excluded of free specific volume
v^*	L-J volumetric scaling parameter
$v_f = v - v_o$	Excluded or free volume
$v_{il}^* = v_{il}^*(X_l)$	Concentration-dependent volumetric matrix interaction parameter
V_{hc}	Hard-core cell volume
V_o	Occupied specific volume
$v_o = 2\pi\sigma^3/3$	Hard core of a molecule
X_i	Site fractions
x_i	Mole fractions
$y = N/B$	Lattice occupied volume fraction
z	coordination number (usually $z = 12$ is used)
z, z_o, z_∞	Distance from clay platelet surface in the orthogonal direction
$zq = s(z-2) + 2$	Number of interchain contacts
Z	Configurational Partition Function (S-S eos)

6.8.2 Greek

$\varepsilon_{il}^* = \varepsilon_{il}^*(X_l)$	Concentration-dependent energetic matrix interaction parameter
$\varepsilon_{ij}^*, v_{ij}^*$	L-J binary interaction parameters
v^*	L-J volumetric scaling parameter
$\xi \equiv P_R^*/P^*$	Ratio of the pressure reducing parameter in flow to P^* : $\xi = 6.81 - 3.82T/T_g$
$\varepsilon, \varepsilon^*$	L-J maximum attractive energy and its scaling form
Δh	Reduction of hole fraction
$\Psi'(s)$	Total partition function
α_i	Thermal expansion coefficient: $\alpha \equiv (\partial \ln V / \partial T)_{P, T^o, q}$
$\delta_\varepsilon, \delta_v$	Adjustable parameters in Eqs. (6.54) and (6.55)
$\delta = \delta(T, P)$	Solubility parameter, $\delta = \sqrt{CED} = \sqrt{C\tilde{E}D \times P^*}$.
ϕ	Clay volume fraction
ϕ_o	Potential energy when the point s -mer is in the cell center
$\eta(\sigma_{12} = \text{const})$	Constant stress shear viscosity
η_0	Zero-shear viscosity
κ	Compressibility coefficient: $\kappa \equiv (\partial \ln V / \partial P)_{T, P^o, q}$
κ_1	Isothermal liquid compressibility

λ	ISM parameter
μ^* and l^*	Reducing variables for molecular dipole moment and length
$\mu_{11}; \mu_{12}$	Polymer-polymer and polymer-gas mixture chemical potentials
ρ, ρ^*	Density, characteristic density
ρ^*, s^*, η^*, c^*	FOV reducing parameters: the “hard-sphere” radius, number of contacts per segment, respectively
ρ^*	Separation distance between centers of neighboring segments
σ_{L-J}	L-J segmental repulsion radius
σ	Standard deviation
ω_α	Acentric factor in Eq. (6.13)
ω	S-S cell volume: $\omega = yV/(Ns)$

6.9 References

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6.10 SUBJECT INDEX

acentric factor, ω_α ,

Benedict, Webb and Rubin (BWR) eos

Cell models: van der Waals; Nanda and Simha; Prigogine cell model & its extension to solutions; DiBenedetto model for polymers;

cohesive energy density (CED): CED in reduced form $\tilde{CED}$; CED for molten polymers

compressibility parameter

configurational thermodynamics,

corresponding states principle (CSP): van der Waals introduction; Prigogine CSP theorem

equation of state (eos): definition; evolution; diversity; eos for polymers; reviews of eos; Flory-Orwoll-Vrij (FOV) eos; Sanchez-Lacombe (S-L); Hartmann and Haque (H-H); Dee and Walsh (D-W “modified cell model” (MCM); comparison with experiments; eos for binary systems; eos for polymer blends; for polymer composites; for polymeric nanocomposites (PNC); eos extension to non-equilibrium states

external degree of freedom $3c$:

free volume: Clausius concept; van der Waals “excluded volume”; effect on flow behavior and viscoelasticity

gas solubility in polymers: S-S equations for binary mixtures; Gibbs free energy of the mixing; magnetic suspension balance measurements

glass transition, $T_g \approx (2/3)T_m$; frozen fraction of free volume (FF); Simha and Robertson stochastic relaxation theory; Angell’s strong and fragile glass-formers; hysical aging: kinetics; effects of nano-particles.

hole models: Eyring; Peek and Hill

Hougen and Watson compressibility factor

Ihm, Song and Mason (ISM) eos

Lennard-Jones (L-J) potential: maximum attractive energy and repulsive volume; 6-12 potential.

mode-coupling theory (MCT) of segmental and structural relaxation

Nies and Stroeks modification of S-S cell-hole model

polymeric nanocomposites (PNC): definitions; applications; performance; PVT ; eos; free volume loss; “hairy clay platelets” (HCP) model;

positron annihilation lifetime spectroscopy (PALS)

Prigogine, Trappeniers and Mathot (PTM) eos for s-mers: Nanda and Simha modification; Arora *et al.* modification;

PVT measurements and surface

Simha-Somcynsky (S-S) cell-hole statistical thermodynamic theory: partition function; equation of state (eos) for a single component; for multicomponent polymeric systems (MPS); hole fraction (h); cohesive energy density (CED); internal pressure, $\tilde{p}_i$; simplification of S-S eos; modification of S-S eos; polynomial expansion;

solidification of organics on high energy surface; surface force analyzer (SFA)

solubility parameter from CED $\delta = \sqrt{CED} = \sqrt{C\tilde{E}D \times P^*}$.

square-well potential (SWP)

surface tension,

Tait eos in reduced variables

transition temperatures at $T > T_g$: Boyer's "liquid-liquid" T_{LL} ; MCM crossover temperature, T_c ; Ngai's crossover temperature, T_B

van der Waals (VDW; 1837-1923): semi-empirical, two-parameter, cubic eos; VDW Eq. in reduced variables; S-S eos in form of the VDW Eq.; modifications of the VDW Eq.; CSP in VDW theory

Williams-Landel-Ferry (WLF) equation

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Thank you.

Sincerely,

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