Fluid Phase Equilibria 321 (2012) 44–48

Contents lists available at SciVerse ScienceDirect

Fluid Phase Equilibria

journal homepage: www.elsevier.com/locate/fluid

# Free volume and cavity formation in molecular liquids

M. Prezhdo[a], L. Loginova[b], V. Zubkova[c], V. Prezhdo[c],*

[a] Department of Chemistry, University of Rochester, Rochester, NY 14627, USA
[b] Department of Analytical Chemistry, Karazin State University, 7 Svoboda Sq., Kharkov 61077, Ukraine
[c] Institute of Chemistry, Jan Kochanowski University, 15G Swietokrzyska Str., 25-406 Kielce, Poland

ARTICLE INFO

*Article history:*
Received 12 October 2011
Received in revised form 21 February 2012
Accepted 21 February 2012
Available online 3 March 2012

*Keywords:*
Cavity formation
Accessible volume
Screened volume
Free volume

ABSTRACT

By considering the theory of cavity formation in molecular liquids we show that general relationships for the accessible volume notably outperform models based on molecular packing. We ascertain several useful correlations between the molecular properties and the values of the accessible and screened volumes, and demonstrate that ordinary liquids boil when the ratio of the accessible and free volumes reaches the same threshold value.

## 1. Introduction

The cavity formation theory of liquids provides one of the most practical and widely used means for explaining substance solubilities [1,2], calculating solvation free energies [3], investigating molecular complexes [4,5], studying structural order [4], characterizing structural relaxation [5], rationalizing fluorescence of solvated chromophores [6], explaining chemical transfer energetics [7], treating statistical thermodynamics of mixtures [8,9] and investigating other properties of liquids [12,13]. For example, the model developed in Ref. [10] based on the cavity formation theory and solute–solvent dispersion components of the non-polar hydration free energy has been employed successfully in the calculation of the mean-force potential for biological solvation [11] and dimerization [12]. The solvent cavity concept is used in many approaches, including the scaled particle theory [13,14], the Lee theory [13], the kinetic theory of nucleation in liquids [14], the homogeneous nucleation theory [15], the theory of hydrophobicity [16,17], and the free volume approach [18]. The process of cavity formation is particularly important for treating the statistical thermodynamics of mixtures [19,20]. In many cases, the properties of the hard sphere fluid form the starting point for the thermodynamic perturbation and variational theories [21,22]. Definition of the cavity size distribution function remains the subject of modern research [23,24]. In this paper we compare simple molecular and statistical models for the cavity volume and demonstrate that models of the latter type give significantly better results. We correlate the accessible and screened volumes with molecular properties and show that the ratio of the accessible to free volume is approximately constant at the boiling point of ordinary liquids.

## 2. Theory

### 2.1. Free volume theories

At the present time free volume theories have received wide acceptance, because they are based on the statistical mechanics, they may be easily extended to multicomponent systems, the using parameters have a precise physical meaning, their equations are simple and involve reduced number of parameters, they can be used over wide ranges of temperature and pressure [25].

The free-volume models can be divided into two main groups. The first one correlates the transport properties, $P$, just with the molar free volume, $V_f$:

$$P = f(V_f) \tag{1}$$

($P$ represents either the self-diffusion coefficient $D$, the viscosity $\eta$ or thermal conductivity $\lambda$). This relation is only valid for fluids without attractive molecular interactions, e.g. hard sphere (HS) and hard convex body fluids.

The second group comprises the so-called hybrid models, which combine the concepts of free volume and activation energy, $E_a$, and can be written as

$$P = f(V_f)\exp\left(-\frac{E_a}{RT}\right) \tag{2}$$

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* Corresponding author. Tel.: +48 41 3257025; fax: +48 41 3497062.
*E-mail address:* victor@ujk.edu.pl (V. Prezhdo).

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doi:10.1016/j.fluid.2012.02.017

where $R$ is the ideal gas constant and $T$ is the absolute temperature. Eq. (2) includes both attractive and repulsive interactions.

To take one example, in the free volume theory [25,26], the self-diffusion coefficient can be obtained by averaging the local one, i.e.,

$$D = \int_{\upsilon^*}^{\infty} \int_{\varepsilon^*}^{\infty} D_{loc} p(\varepsilon') p(\upsilon_{loc}) d\upsilon_{loc} d\varepsilon \tag{3}$$

where $D_{loc}$ is the local diffusion coefficient which is a function of local free volume $\upsilon_{loc}$ and molecular local energy $\varepsilon'$, $\upsilon^*$ is the molecular critical local free volume, $\varepsilon^*$ is the molecular critical local energy, $p(\varepsilon')$ and $p(\upsilon_{loc})$ are, respectively, the molecular local energy and free volume density functions. $p(\varepsilon')$ and $p(\upsilon_{loc})$ have the following forms:

$$p(\varepsilon) = \frac{1}{2kT} \left( \frac{\varepsilon'}{kT} \right)^2 \exp\left( -\frac{\varepsilon'}{kT} \right) \tag{4}$$

$$p(\upsilon_{loc}) = \frac{\gamma}{\upsilon_f} \exp\left( -\frac{\gamma \upsilon_{loc}}{\upsilon_f} \right) \tag{5}$$

In Eqs. (4) and (5), $k$ is the Boltzmann constant, $T$ is the absolute temperature, $\upsilon_f$ is the free volume per molecule and $\gamma$ is a numerical factor whose value lies between 0.5 and 1.0.

Generally, the local diffusion coefficient is assumed to be proportional to the molecular local free volume $\upsilon_{loc}$. Now, there is a problem to calculate $\upsilon_{loc}$, the problem which has been solved for 65 years since Frank suggested the formula (6) [27]. According to Frank, the free volume can be approximated by the residual entropy $S^R$, i.e.,

$$\frac{\upsilon_f}{\upsilon} = \frac{1}{\Delta} \exp\left( -\frac{S^R}{kT} \right) \tag{6}$$

where $\Delta$ is a constant.

The free volume consists of both the microcavities and the space explored by the molecules during their thermal fluctuations away from the equilibrium position $r_0$ to $r > r_0$. Not all of $V_f$ can be accessible to the motion of particles at a given moment of time. In order to penetrate into some parts of $V_f$, significant energy barriers produced by the surrounding atoms and molecules must be overcome. Screened areas of that kind can form within a molecule, for example in cyclic compounds, as well as at molecular boundaries, for instance between non-bonded atoms of the same molecule. Particularly significant contributions to this screened volume ($V_{scr}$) can be created in the form of screened microcavities between particles as they approach and re-orient towards each other.

Free from those faults is the volume accessible to movement of microparticles in a liquid, the so-called accessible volume ($V_{ac}$).

### *2.2. Volume accessible to movement of microparticles*

The volume accessible to movement of microparticles in a liquid, the so-called accessible volume ($V_{ac}$), is the key parameter governing cavity formation [28]. It is a common part of the calculations of the equilibrium and kinetic properties of liquids according to the statistical [29] and kinetic [18] theories. The $V_{ac}$ value enters the van der Waals equation, the Bachinski formula for viscosity [30], and the configuration integral $z_{conf} = (V_{ac})^N e^{-E/RT}$ [31]. Therefore, it is particularly important to elucidate the factors that determine the magnitude of the accessible volume and to obtain reliable equations for its calculation.

One of the simplest formulas for the calculation of the accessible volume, the Eyring–Herschfelder equation proposed in 1937 [32] remains useful to these days:

$$V_{ac} = C^3 (V_l^{1/3} - \sigma)^3 \tag{7}$$

Here, $C^3$ stands for the coordination number, $V_l$ is the volume estimated for a single molecule in a liquid, and $\sigma$ is the diameter of the molecule. Using the approximate partition function of a liquid

$$z_l = \frac{1}{N!} \left[ \left( \frac{2\pi mkT}{h^2} \right)^{3/2} V_{ac} \right]^N (z_{\text{int}} e^{-E/RT})^N,$$

in combination with the following statistical expression

$$\left( \frac{\partial S}{\partial V} \right)_T = \left( \frac{\partial p}{\partial T} \right)_V = R \left( \frac{\partial \ln V_{ac}}{\partial V} \right)_T, \tag{8}$$

$$p_{external} = RT \left( \frac{\partial \ln V_{ac}}{\partial V} \right)_T - \left( \frac{\partial E}{\partial V} \right)_T, \tag{9}$$

Eq. (7) allows one to calculate the accessible volume from the values for the coordination number ($C^3$), and the molar volume ($V$), along with the compression ($\beta$) and expansion ($\alpha$) coefficients:

$$V_{ac} = \frac{4\pi C^3}{3V^2} \left[ R \frac{\beta}{\alpha} \right]^3. \tag{10}$$

Alternatively, one can use the value of the heat of evaporation $\Delta H$:

$$V_{ac} = C^3 V \left[ \frac{RT}{\Delta H - RT} \right]^3. \tag{11}$$

The accessible volumes obtained from Eqs. (4) and (5) for very different types of liquids with $C^3 \approx 8$–10 fall within the rather narrow range of 0.1–0.7 cm$^3$/mol [32,33], see Table 1. Similar $V_{ac}$ values, Table 2, are obtained using the Lennard–Jones formula [34]:

$$V_{ac} = 2\pi a^3 g,$$

and assuming the simple cubic packing of the particles:

$$V_{ac} = 8.85 V g. \tag{12}$$

The integral $g = \int_0^{\rho_M} e^{-z\psi(\rho)/kT} 2\rho^2 d\rho$ in the equation above for various values of $V/Nr_0^3$ and $kT/\varepsilon_0$ can be found in the tables of Ref. [35].

The accessible volume values obtained from these formulas appear, as a rule, an order of magnitude smaller than those calculated from the viscosity data (Table 1). They are also 10-fold smaller than the values calculated from the radial distribution function. For example, for Ar $V_{ac}/V = 0.01$ according to the above equations, while this ratio obtained using the radial distribution function is equal to 0.14 [36]. Further, one would expect that the increase of the system volume due to melting [37] should be determined primarily by the accessible volume of molecules in the liquid phase [28]. However, the values of the accessible volume calculated using the above equations are significantly smaller than the volume increase during the solid/liquid phase transition [38].

The dependences considered above do not take into account the whole volume accessible to molecular motion in a liquid, because the models used to derive these expressions are over simplistic [39]. Apparently, these models account only for thermal motions of the molecular center of mass, the so-called fluctuation volume [39], which is equal to $(N/\upsilon^3)[kT/2\pi m]$ [28]. The fluctuation volume never exceeds a few tens of cm$^3$/mol even at high temperatures. Moreover, the equations considered above should be limited to substances composed of spherically symmetric and non-polar particles and cannot fully describe the influence of more complex molecular properties on the $V_{ac}$ values.

Calculations of the accessible volume can be approached based on the most general characteristics of a liquid, namely, the absence of the long-range order and the presence of density fluctuations and