Free Volume and Density and Temperature Dependence of Diffusion Coefficients of Liquid Mixtures

Kyunil Rah and Byung Chan Eu

Department of Chemistry and Centre for the Physics of Materials, McGill University,
801 Sherbrooke Street West, Montreal, Quebec H3A 2K6, Canada

A simple formula for the diffusion coefficient of liquid mixtures, expressed in terms of the work necessary to create a characteristic free volume in the liquid, is presented in the spirit of the Arrhenius activation theory and tested in comparison with available experimental data. If use is made of the generic van der Waals equation of state, the free volume appearing in the formula for the diffusion coefficient can be expressed in terms of the equilibrium pair correlation functions. The theoretical values for diffusion coefficients agree excellently with experimental values with regard to the density and temperature dependence of the diffusion coefficients of argon and krypton.

Self-diffusion coefficients and diffusion coefficients are basic transport coefficients, in terms of which other transport coefficients can be expressed. A typical example is the Stokes-Einstein relation. Similar relations have been shown to hold for the bulk viscosities and thermal conductivities of monatomic and diatomic liquids in recent papers [1] . Despite their importance in such phenomena the statistical mechanical theories of diffusion coefficients are not well developed at present and the only reliable alternative lies in molecular dynamics simulation methods [2]. Although free volume theories of diffusion have been around in literature [3–6] for a long time, the difficulty associated with defining the free volume in a rigorous and practical form and calculating it in a reliable accuracy by statistical mechanics has rendered them impractical to use for gaining molecular understanding of diffusion and relating them to experiment.

The Cohen-Turnbull (CT) theory [6] is a free volume theory that yields the self-diffusion coefficient D of a simple liquid in the form

$$D = g_{CT} \exp(-\alpha v^c / v_f), \qquad (1)$$

where v_f is the free volume per molecule, v^c the characteristic free volume per molecule, α an adjustable parameter, and $g_{CT} = g a(\rho) \overline{c}$ with g denoting the geometric factor, $a(\rho)$ a quantity that is roughly the diameter of the cage created in the liquid, and $\overline{c}$ the mean gas kinetic speed. Since g_{CT} is akin to the mean free path expression for the self-diffusion coefficient of the gas, in a recent paper [7] on self-diffusion coefficients of simple liquids we have identified it with the Chapman-Enskog (CE) self-diffusion coefficient D_0, which may be further approximated by the self-diffusion coefficient D_{hs}^0 [8] of a hard sphere gas: $g_{CT} \equiv D_0 \simeq D_{hs}^0 = 1.019(3/8\rho\sigma^2)\sqrt{k_B T/\pi m}$, where k_B is the Boltzmann constant, ρ is the density, and σ is the diameter of the molecule of mass m. This identification yields D in the form

$$D = D_0 \exp(-\alpha v^c / v_f). \qquad (2)$$

Even with this identification of g_{CT} with either D_0 or D_{hs}^0, formula (2) does not yield $D(\rho, T)$ unless v_f is known in terms of ρ and T as well as molecular parameters characteristic of the liquid in question.

We have shown in Ref. [7] that v_f can be calculated rigorously by statistical mechanics with the help of the generic van der Waals (GVDW) equation of state [9]

$$[p + A(\rho, T)\rho^2][1 - B(\rho, T)\rho] = \rho k_B T, \qquad (3)$$

where p is the pressure, and $A(\rho, T)$ and $B(\rho, T)$, generally depending on ρ and T, are called the GVDW parameters which are given in terms of the pair correlation function and, in the low density limit, reduce to the original van der Waals parameters a and b in the van der Waals equation of state $(p + a\rho^2)(1 - b\rho) = \rho k_B T$. Equation (3) is rigorously equivalent to the virial equation of state. Its derivation will be indicated for the case of a binary liquid mixture later. The parameter B in particular is closely related to the positive repulsive potential energy and therefore is a good measure of the excluded volume. Therefore the free volume v_f can be defined in terms of B:

$$v_f = v[1 - B(\rho, T)\rho], \qquad (4)$$

where $v = 1/\rho$, the specific volume. Thus, if we identify v^c with the molecular volume $v_0 = \pi\sigma^3/6$, then with the help of Eqs. (3) and (4) D in Eq. (1) can be written as

$$D = D_0 \exp(-W/k_B T), \qquad (5)$$

$$W = \alpha v_0 [p + A(\rho, T)\rho^2], \qquad (6)$$

where D_0 may be replaced by D_{hs}^0 in the CE kinetic theory. In this manner, with $g_{CT} = D_0$, $v^c = v_0$, and the definition of v_f by Eqs. (3) and (4), the self-diffusion coefficient D in the CT theory is now fully elevated to the level of a statistical mechanical theory, except for the adjustable parameter α, which was found to be about unity [7] and independent of ρ but weakly dependent on T. In Ref. [7] formula (5) was shown to be excellent in accuracy with regard to the density and temperature dependence of D.

The quantity W in the exponential factor in Eq. (5) is the work required to create a characteristic void of volume αv_0 in the liquid under the effective (net) pressure $p_{\text{eff}} = p + A(\rho, T)\rho^2$ in the liquid and therefore $P_{v_0} \equiv \exp(-W/k_B T)$ is the probability of creating such a void in the liquid into which a particle is displaced, and as a result diffusion occurs. Consequently, the self-diffusion coefficient D of the liquid is proportional to P_{v_0} and the proportionality constant is the gas phase diffusion coefficient D_0 to which D tends in the limit of vanishing density, where the ideal gas equation of state holds. This interpretation suggests that W may be regarded as the activation energy for diffusion, and one may thus regard Eq. (5) as the expression for self-diffusion coefficient in the Arrhenius theory of activation [10] for diffusion in which the activation energy for diffusion is defined by work W to create volume αv_0. This argument shows that with the argument leading to Eq. (5) from Eq. (1) the CT theory can be turned into an Arrhenius theory of activation for diffusion.

In this Letter we show that within the spirit of the Arrhenius activation theory the formula for D in Eq. (5) can be readily generalized to liquid mixtures. In the case of a binary simple liquid mixture, we show that the formula for diffusion coefficient

$$D_{12} = D_{12}^0 \exp\{-v_{12}^c[p + A(\rho,T)\rho^2]/k_B T\}, \quad (7)$$

where D_{12}^0 is the Chapman-Enskog diffusion coefficient for the gas mixture in the normal state and v_{12}^c is the mean characteristic volume (void) to be defined explicitly together with the more precise meaning of the GVDW parameter A for the mixture, gives an excellent temperature and density (or composition) dependence for diffusion coefficients, when compared with the experimental data. This formula in fact can be derived from a molecular theory consideration, the details of which will be given elsewhere because of the space limitation. The main aim of this Letter is to communicate the capability of this simple formula for calculating diffusion coefficients of liquids by using statistical mechanics methods only.

The characteristic free volume v_{12}^c in the case of a binary mixture is given by

$$v_{12}^c = \alpha_1 v_1^0 X_1 + \alpha_2 v_2^0 X_2, \quad (8)$$

where α_i $(i = 1, 2)$ are the same adjustable parameters appearing in the CT theory [6] for single-component liquids [i.e., Eq. (1)] and therefore no longer free, $v_i^0 = \pi \sigma_i^3/6$ is the molecular volume of species i, and $X_i = \rho_i/\rho$ with $\rho = \rho_1 + \rho_2$, the mole fraction of i, with ρ_i denoting the number density of species i. Therefore it is asserted that v_{12}^c given in Eq. (8) is a mean value of volumes proportional to the molecular volumes of the species of the mixture.

To justify the definition of v_f given earlier, we now turn to the GVDW equation of state for a binary mixture contained in volume V and at temperature T. The virial equation of state for the mixture is given by

$$\frac{\beta p}{\rho} = 1 - \frac{2\pi\beta}{3\rho} \sum_{i,j=1}^{2} \rho_i \rho_j \int_0^\infty dr\, r^3 u_{ij}'(r)$$
$$\times e^{-\beta u_{ij}(r)} y_{ij}(r), \quad (9)$$

where $\beta = 1/k_B T$. Here $u_{ij}(r)$ is the potential energy between pair ij and $u_{ij}' = du_{ij}/dr$. The cavity function $y_{ij}(r)$ is defined as usual by $y_{ij}(r; \rho_1, \rho_2, T) = \exp[\beta u_{ij}(r)]g_{ij}(r; \rho_1, \rho_2, T)$, where $g_{ij}(r)$ is the pair correlation function.

If the potential energy $u_{ij}(r)$ has a zero at $r = \sigma_{ij}$, where σ_{ij} is finite, then the integral in Eq. (9) can be split into two parts, one involving the positive repulsive branch and the other involving the negative part of the potential energy. Thus with the definitions of the integrals

$$A_{ij} = \frac{2\pi}{3} \int_{\sigma_{ij}}^\infty dr\, r^3 u_{ij}'(r) \exp[-\beta u_{ij}(r)]y_{ij}(r), \quad (10)$$

$$B_{ij} = -\frac{2\pi\beta}{3} \int_0^{\sigma_{ij}} dr\, r^3 u_{ij}'(r) \exp[-\beta u_{ij}(r)]y_{ij}(r), \quad (11)$$

and the abbreviations

$$A = \sum_{i,j=1}^{2} A_{ij}(\rho, T)X_i X_j, \quad (12)$$

$$B = \frac{\sum_{i,j=1}^{2} B_{ij}(\rho, T)X_i X_j}{1 + \rho \sum_{i,j=1}^{2} B_{ij}(\rho, T)X_i X_j}, \quad (13)$$

the virial equation of state (9) can be rearranged to the GVDW equation of state given in Eq. (3). The rearrangement involved is exact. Note that in the case of a single-component liquid the sums over indices i and j are absent. Since B_{ij} and thus B are positive and associated with the repulsive core of the molecules, the $B\rho$ term in the GVDW equation of state (3) represents the fraction of the excluded volume and it therefore is natural to define the free volume v_f by the formula given in Eq. (4). Equations (11) and (13) give the statistical mechanical representation for the free volume of a binary mixture. On use of v_f so defined as in Eq. (4), the diffusion coefficient in Eq. (7) may be written in a form reminiscent of the CT theory D given in Eq. (2),

$$D_{12} = D_{12}^0 \exp\{-v_{12}^c/v_f\}. \quad (14)$$

Therefore, to calculate the density and temperature dependence of D_{12} there remain the tasks of calculating D_{12}^0 and the cavity functions $y_{ij}(r)$. For the simplicity of the formula, we propose to use for D_{12}^0 the CE diffusion coefficient for a binary hard sphere mixture: $D_{12}^0 = (3/8\rho\sigma_{12}^2)\sqrt{k_B T(m_1 + m_2)/2m_1 m_2}$, where m_1 and m_2 are masses. A nonhard sphere result can be used for D_{12}^0 at the cost of a more complicated formula. We believe that in the case of liquids the hard sphere formula is more appropriate and also sufficient.

The pair correlation functions can be calculated by means of a suitable integral equation for the pair correlation functions, such as the Percus-Yevick integral equations, or the Monte Carlo simulation method with a suitable interaction potential model. In this Letter, we have used a Monte Carlo simulation method with a square well potential model for u_{ij}: $u_{ij}(r) = \infty$ for $r < \sigma_{ij}$; $-\varepsilon_{ij}$ for $\sigma_{ij} < r < \lambda_{ij}$; 0 for $r > \lambda_{ij}$. The potential parameters are $\sigma_{Ar} = 0.316$ nm, $\varepsilon_{Ar} = 69.4 k_B$, $\lambda_{Ar} = 1.85\sigma_{Ar}$ for argon; $\sigma_{Kr} = 0.336$ nm, $\varepsilon_{Kr} = 98.3 k_B$, $\lambda_{Kr} = 1.85\sigma_{Kr}$ for krypton; and $\sigma_{N_2} = 0.329$ nm, $\varepsilon_{N_2} = 53.7 k_B$, $\lambda_{N_2} = 1.87\sigma_{N_2}$ for nitrogen, considered in this work. The potential parameters for cross potentials (e.g., u_{ArKr}) are calculated by using the combining rules: $\sigma_{12} = (\sigma_1 + \sigma_2)/2$, $\varepsilon_{12} = \sqrt{\varepsilon_1 \varepsilon_2}$, and $\lambda_{12} = (\lambda_1 + \lambda_2)/2$, for the size, well depth, and range parameter, respectively.

In Fig. 1, D_{12} is plotted against X_{Ar} for liquid argon-krypton mixtures at $T = 121$ K and reduced density $\rho^* = 0.62$. Here $\rho^* = \rho\sigma_{12}^3$. The theoretical values are calculated by using the pair correlation functions obtained by means of a Monte Carlo method with the potential parameters specified earlier. The line, drawn to guide the eyes, is a least squares fit to the theoretical values of the present theory, represented by open circles. Other symbols are the molecular dynamics (MD) simulation results by Zhou and Miller [11] and by Heyes [12]. The MD results of Zhou and Miller and Heyes differ probably owing to the difference in simulation times. The maximum simulation times of Zhou and Miller are in the range of $t_{max} = 20 \sim 80$ ps, whereas that of Heyes is $t_{max} = 2.5$ ps. The present theoretical results are found to be in good agreement with the MD results by Zhou and Miller, whereas the agreement
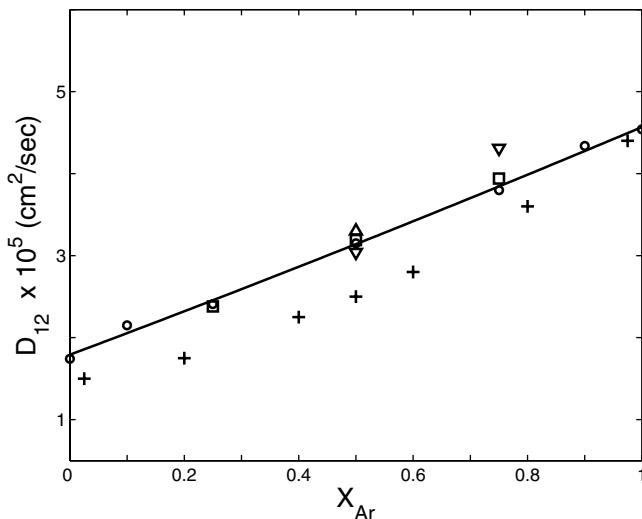
with Heyes' results is only qualitative. We could not find experimental data on simple liquid mixtures to use for comparison.

The tracer diffusion coefficient is obtained from the expression for D_{12} given in Eq. (14) in the limit of either $X_1 \to 0$ or $X_2 \to 0$. For example, in the limit of $X_2 \to 0$ the tracer diffusion coefficient of species 2 is given by

$$D_t(2) = D_{12}^0 \exp(-\alpha_1 v_1^0/v_f). \qquad (15)$$

This is the diffusion coefficient of a trace amount of species 2 in the solvent of species 1. It should be emphasized that it is not the self-diffusion coefficient of species 2. In Fig. 2a $D_t(Ar)$ for argon in liquid N_2 is plotted against T and ρ. The pressure is fixed at $p = 0.92$ atm and the nitrogen density ranges from 0.806 to 0.865 g/cm^3. We have used $\alpha_{N_2} = 1.1$ determined from the data of Ref. [16]. The solid curve is drawn to guide the eyes through the theoretical values for $D_t(Ar)$, represented by open circles. The other symbols are the experimental data [13]. The upper scale of the figure indicates the density dependence of $D_t(Ar)$. In Fig. 2b $D_t(Kr)$ for krypton in liquid argon is examined in the temperature range 84 K $\leq T \leq 100$ K and the density range 1.31 g/cm^3 $\leq \rho_{Ar} \leq 1.41$ g/cm^3 along the coexisting line of liquid argon. The solid curve, which is a least

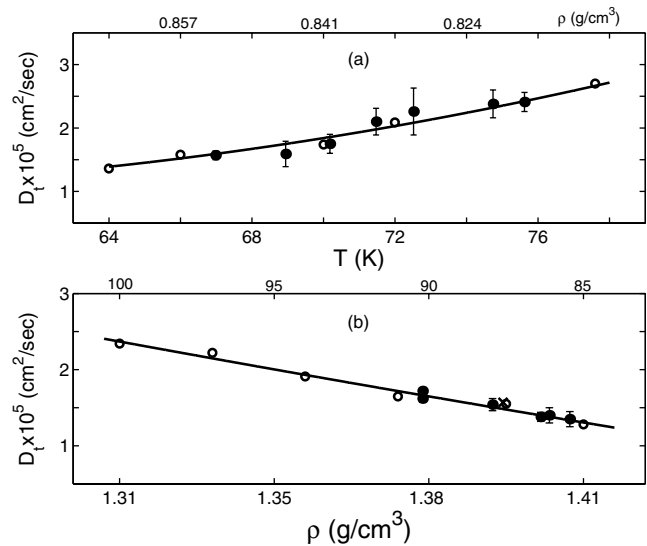FIG. 2. (a) $D_t(Ar)$ vs T (or ρ) for Ar in liquid N_2 in the temperature (density) range of 64 K $\leq T \leq 78$ K (0.865 g/cm^3 $\geq \rho_{N_2} \geq 0.806$ g/cm^3) and $p = 0.9$ atm. The open circles ($\bigcirc$) indicate the theoretical values for $D_t(Ar)$ and the solid curve is drawn to guide the eyes. The filled circles ($\bullet$) are the experimental data [13]. The ρ dependence is indicated in the upper scale of the figure. (b) $D_t(Kr)$ vs ρ (or T) for Kr in liquid Ar in the temperature (density) range 84 K $\leq T \leq 100$ K (1.131 g/cm^3 $\geq \rho_{Ar} \geq 1.141$ g/cm^3) along the coexisting line of liquid argon. The open circles ($\bigcirc$) are the theoretical values and the solid line is their least squares fit. The filled circles ($\bullet$) are the experimental data from Ref. [14], and the cross ($\times$) from Ref. [15].

FIG. 1. The composition dependence of D_{Ar-Kr} of the liquid Ar-Kr mixtures at $T = 121$ K and $\rho^* = 0.62$. The open circles ($\bigcirc$) indicate the theoretical values and the solid curve is drawn to guide the eyes. The crosses ($+$) are the MD results from Ref. [12], and the other symbols ($\triangle, \square, \triangledown$) are for the MD results from Ref. [11].

squares fit to the theoretical values, is also drawn to guide the eyes. The experimental values are from Refs. [14,15]. The upper scale of the figure indicates the T dependence of $D_t(\text{Kr})$. The values for α_{Ar}, α_{Kr}, and α_{N_2} used for the tracer diffusion coefficients were $\alpha_{\text{Ar}} = \alpha_{\text{Kr}} = 1$ and $\alpha_{\text{N}_2} = 1.1$, which were taken from the values used for the self-diffusion coefficients [7,16]. Therefore, they are not free parameters chosen to fit the data for these two figures. Comparison with experiment made in the two figures indicates that the present theory works well for highly packed liquids at low temperature. To give an idea about the proximity of the density and temperature range to the freezing point we quote the triple points of N_2 and Ar: $T_t = 63.15$ K, $\rho_t = 0.868$ g/cm^3 for N_2 and $T_t = 83.81$ K, $\rho_t = 1.417$ g/cm^3 for Ar, both of which are rather close to the range of density and temperature examined here.

Since experimental data on diffusion coefficients of simple liquid mixtures are scarce, the comparison of theory and experiment made to test the theoretical formula presented in this work is limited, but where comparison is made the agreement between theory and experiment or simulations is found to be excellent. Therefore, with the formula presented earlier it is now possible to calculate diffusion coefficients of simple liquid mixtures by means of statistical mechanics methods alone. This has been made possible by combining the ideas of the free volume theory, the GVDW equation of state which provides the statistical mechanical representation of free volume in an exact manner, and the use of the CE formula for D_{12}^0. The diffusion coefficient presented also reduces to the self-diffusion coefficient reported previously, if the single-component limit is taken in the diffusion coefficient of the mixture. The diffusion coefficient presented and the self-diffusion coefficient derivable from the former or presented in Ref. [7] can also be used to perform completely statistical mechanical calculations of shear viscosity, bulk viscosity, and thermal conductivity of liquids by means of the theories described in Ref. [1], where they were used as the empirical inputs for lack

of statistical mechanical theories for them. We believe that they can be also applied to the study of supercooled liquids [17] and liquid metals [18]. In such applications lies the practical significance of the Arrhenius activation theory formula (7) for the diffusion coefficient presented.

[1] K. Rah and B.C. Eu, Phys. Rev. Lett. **83**, 4566 (1999); Phys. Rev. E **60**, 4105 (1999); J. Chem. Phys. **112**, 7118 (2000); **114**, 10436 (2001); **115**, 9370 (2001).
[2] M.P. Allen and D.J. Tildesley, *Computer Simulation of Liquids* (Clarendon, Oxford, 1987).
[3] A.J. Batschinsky, Z. Phys. Chem. **84**, 644 (1913).
[4] H. Eyring, J. Chem. Phys. **4**, 283 (1936).
[5] A.K. Doolittle, J. Appl. Phys. **22**, 1471 (1951).
[6] M.H. Cohen and D. Turnbull, J. Chem. Phys. **31**, 1164 (1959).
[7] K. Rah and B.C. Eu, J. Chem. Phys. **115**, 2634 (2001).
[8] S. Chapman and T.G. Cowling, *The Mathematical Theory of Nonuniform Gases* (Cambridge, London, 1970), 3rd ed.
[9] B.C. Eu and K. Rah, Phys. Rev. E **63**, 031203 (2001).
[10] S. Arrhenius, Z. Phys. Chem. **4**, 226 (1889).
[11] Y. Zhou and G.H. Miller, Phys. Rev. E **53**, 1587 (1996).
[12] D.M. Heyes, J. Chem. Phys. **96**, 2217 (1992).
[13] G. Cini-Castagnoli, G. Pizzella, and F.P. Ricci, Nuovo Cimento **10**, 300 (1958).
[14] G. Cini-Castagnoli and F.P. Ricci, Nuovo Cimento **15**, 795 (1960).
[15] P.J. Dunlop and C.M. Bignell, J. Chem. Phys. **108**, 7301 (1998).
[16] K. Krynicki, E.J. Rahkamaa, and J.G. Powles, Mol. Phys. **28**, 853 (1974).
[17] See, for example, the review article by U. Mohanty, Adv. Chem. Phys. **89**, 89 (1995).
[18] M. Asta, D. Morgan, J.J. Hoyt, B. Sadigh, J.D. Althoff, D. de Fontaine, and S.M. Foiles, Phys. Rev. B **59**, 14271 (1999).