Self-Diffusion Coefficients of Lennard-Jones Liquids and Gases for Various Models in the Modified Free Volume Theory: Tables

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Abstract

We present tables for self-diffusion coefficients of the Lennard-Jones liquids and gases for various model formulas in the modified free volume theory of diffusion in the case of reduced temperatures $T^* = 6.0, 4.0, 1.3, 1.0, 0.8, 0.7$ with reduced density ranging from $\rho^* = 0.025$ to 1. Their accuracies are compared with the molecular dynamic simulation results. In the gas and liquid density regimes, the formula $D_{CERC}$ for the self-diffusion coefficient is accurate within maximum 4% of the molecular dynamics simulation values reported in the literature. It is the most reliable among the formulas presented.

1 Self-Diffusion Coefficients of the Lennard-Jones Fluids

In this note, the self-diffusion coefficients are tabulated for Lennard-Jones (LJ) fluids, which are calculated with various model formulas in the modified free volume (MFV) theory[1]. The reduced temperatures studied are $T^* = 6.0, 4.0, 1.3, 1.0, 0.8, 0.7$ and the reduced density ranges from $\rho^* = 0.025$ to $\rho^* = 1$. Here $T^* = k_B T/\epsilon$ and $\rho^* = \rho \sigma^3$, where $\epsilon$ is the well depth and $\sigma$ is the contact diameter of the LJ fluid, $k_B$, $T$, and $\rho$ denoting, respectively, the Boltzmann constant, temperature, and number density. The various formulas in the MFV theory of diffusion computed in this article are modifications of the original form for the self-diffusion coefficient of simple fluids in the MFV theory[1]:

$$D = \frac{3}{8 \rho \sigma^2} \sqrt{\frac{k_B T}{\pi m}} \exp\left(-\alpha v_0/v_f\right),$$

where $v_f$ is the mean free volume, $v_0$ is the critical volume, and $\alpha$ is the free volume overlap parameter. In the MFV theory, the mean free volume $v_f$ is given
by the generic van der Waals (GvdW) equation of state\textsuperscript{2}, which was originally identified with the formula
\begin{equation}
\frac{v}{v_0} = \left[1 - \frac{2\pi}{3}\beta \rho \int_0^{r^*} dr r^3 \frac{du}{dr} g(r, \rho, T)\right]^{-1}
\end{equation}
with \(u\) denoting the intermolecular interaction potential, e.g., the LJ potential; \(g(r, \rho, T)\) the pair correlation function (radial distribution function); and \(\beta = 1/k_B T\). The critical volume was originally taken \(v_0 = \pi \sigma^3 / 6\), the covolume of hard spheres of diameter \(\sigma\). The overlap parameter was chosen suitably, usually slightly less than unity, as an adjustable parameter. In the following, this basic formula is suitably modified such that the self-diffusion coefficient is expressible in terms of molecular parameters only, yet in sufficiently good accuracy for the self-diffusion coefficient.

### 1.1 Model \(D_{HS}\)

With the definition of \(r^\dagger\) as the maximum position of the function
\begin{equation}
I(r) = -r^3 \frac{du}{dr} g(r, \rho, T),
\end{equation}
that is,
\begin{equation}
\left(\frac{dI}{dr}\right)_{r=r^\dagger} = -\left[\frac{d}{dr} r^3 \frac{du}{dr} g(r, \rho, T)\right]_{r=r^\dagger} = 0,
\end{equation}
the mean free volume \(v_f\) is modified to the formula
\begin{equation}
\frac{v}{v_0} = \left[1 - \frac{2\pi}{3}\beta \rho \int_0^{r^\dagger} dr r^3 \frac{du}{dr} g(r, \rho, T)\right]^{-1}
\end{equation}
and at the same time \(\alpha v_0\) in Eq. (1) is set
\begin{equation}
\alpha v_0 \Rightarrow \frac{\pi}{6} r_0^{13} \equiv v^c.
\end{equation}
Thus the self-diffusion coefficient takes the form\textsuperscript{3}
\begin{equation}
D_{HS} = \frac{3}{8\rho \sigma^2} \sqrt{\frac{k_B T}{\pi m}} \exp\left(-\frac{v^c}{v_f}\right),
\end{equation}
which is now free from adjustable parameters. It improves the accuracy of the self-diffusion coefficient considerably.

### 1.2 Model \(D_{HSRC}\)

The diameter \(r^\dagger\) a little exaggerates the excluded volume for the LJ fluid. To rectify this feature the diameter of the excluded volume is modified by the following formula\textsuperscript{3}
\begin{equation}
r_e = r^\dagger - |r_{fm} - r_{pm}| \simeq r^\dagger - 0.1222 \sigma.
\end{equation}
Here $r_{fm}$ is the minimum position of $I(r)$ and $r_{pm}$ is the minimum of the potential energy or the zero of the intermolecular force. If the free volume overlap parameter $\alpha$ is taken as $\alpha = (r_c/r^\dagger)^3$, which may be interpreted as the ratio of the volume of a sphere of diameter $r_c$ to that of a sphere of diameter $r^\dagger$, then the critical volume turns out to be simply equal to

$$\alpha v_0 \Rightarrow \frac{\pi}{6} r_c^3 \equiv v^0.$$  

We keep the mean free volume $v_f$ as in Eq. (5). With Eq. (9) for the critical volume facilitating diffusion the self-diffusion formula now takes the form

$$D_{HSRC} = \frac{3}{8\rho\sigma^2} \sqrt{\frac{k_BT}{\pi m}} \exp(-v^0/v_f),$$

which is free from an adjustable parameter.

1.3 Model $D_{CE}$

The pre-exponential factor in the self-diffusion coefficient formulas given earlier represents the self-diffusion coefficient of a hard sphere fluid. However, it appears to be a poor approximation in the low density regime to use a hard sphere diameter in it. To rectify this defect, we replace the hard sphere diameter $\sigma$ with the corresponding Chapman–Enskog collision bracket integral for self-diffusion. Thus we insert the reduced Chapman–Enskog collision bracket integral $\Omega^{(1,1)}$ into Eq. (10) and obtain the formula for the self-diffusion coefficient in the form

$$D_{CE} = \frac{3}{8\rho\sigma^2\Omega^{(1,1)}} \sqrt{\frac{k_BT}{\pi m}} \exp(-v^c/v_f),$$

where $\bar{r} r^\dagger^3 \equiv v^c$ as in Eq. (7). This form corrects the low density behavior.

1.4 Model $D_{CERC}$

This model $D_{CE}$ can be modified slightly if $v^c$ is replaced by $v^0$ introduced in Eq. (9). We obtain

$$D_{CERC} = \frac{3}{8\rho\sigma^2\Omega^{(1,1)}} \sqrt{\frac{k_BT}{\pi m}} \exp(-v^0/v_f),$$

where $v^0$ is defined by Eq. (8) and $v_f$ by Eq. (5). Therefore the relation of $D_{CERC}$ to $D_{HSRC}$ is summarizable in the form

$$D_{CERC} = \frac{D_{HSRC}}{\Omega^{(1,1)}}.$$ 

The various models presented above are used to compute self-diffusion coefficients and compared with the results by the molecular dynamics simulation
results of $D_{MD}$. The results of comparison are presented in the following Tables 1–6, where

$$
\Delta_{CERC} = \frac{D_{CERC} - D_{MD}}{D_{MD}} \equiv \frac{D_{CC} - D_{MD}}{D_{MD}} = \Delta_{CC},
$$

$$
\Delta_{HSRC} = \frac{D_{HSRC} - D_{MD}}{D_{MD}} \equiv \frac{D_{HC} - D_{MD}}{D_{MD}} = \Delta_{HC}, \text{ etc.}
$$

$D_{MD}$ denotes the molecular dynamics simulation value for the self-diffusion coefficient. Self-diffusion coefficients $D_{CERC}$ and $D_{HSRC}$ are abbreviated as $D_{HC} \equiv D_{HSRC}$ and $D_{CC} \equiv D_{CERC}$ for the sake of formatting the Tables suitably.

Among the formulas presented, $D_{CERC}$ works best in the density regime of $\rho^* \approx 0.7$ with a maximum error of 4%, compared with the MD simulation results. Therefore $D_{CERC}$ may be used to study related properties of liquids or gases obeying the LJ interaction law. In the density regime higher than $\rho^* \approx 0.7$ none of the models performs as well; for example, the errors of $D_{CERC}$ tend to be 20 to 40% and the errors of other models are comparable. In this regard, it should be noted that the MD simulations results in the high density regime are rather small and tend to be less reliable. At least, the models studied yield self-diffusion coefficients of a correct order of magnitude and thus may be still useful qualitative studies.
Table 1: Self Diffusion Coefficient of the LJ fluid, $T^* = 6.0$, $\Omega^{(1,1)} = 0.812$

| $\rho$ | $D_{MD}$ | $D_{CC}$ | $\Delta_{CC}$ | $D_{CE}$ | $\Delta_{CE}$ | $D_{HC}$ | $\Delta_{HC}$ | $D_{HS}$ | $\Delta_{HS}$ |
|--------|----------|----------|---------------|----------|---------------|----------|---------------|----------|---------------|
| 0.025  | 25.347   | 25.349   | 0.000         | 25.214   | −0.005        | 20.593   | −0.188        | 20.484   | −0.192        |
| 0.050  | 12.487   | 12.606   | 0.010         | 12.437   | −0.004        | 10.241   | −0.180        | 10.103   | −0.191        |
| 0.075  | 8.181    | 8.324    | 0.018         | 8.097    | −0.010        | 6.763    | −0.173        | 6.578    | −0.196        |
| 0.100  | 6.016    | 6.235    | 0.036         | 6.025    | 0.001         | 5.066    | −0.158        | 4.895    | −0.186        |
| 0.150  | 3.900    | 4.108    | 0.053         | 3.873    | −0.007        | 3.337    | −0.144        | 3.146    | −0.193        |
| 0.200  | 2.850    | 3.020    | 0.060         | 2.648    | −0.071        | 2.454    | −0.139        | 2.151    | −0.245        |
| 0.250  | 2.218    | 2.370    | 0.068         | 2.005    | −0.096        | 1.925    | −0.132        | 1.628    | −0.266        |
| 0.300  | 1.793    | 1.943    | 0.084         | 1.546    | −0.138        | 1.579    | −0.120        | 1.256    | −0.300        |
| 0.350  | 1.492    | 1.629    | 0.092         | 1.194    | −0.200        | 1.323    | −0.113        | 0.970    | −0.350        |
| 0.400  | 1.267    | 1.405    | 0.109         | 0.875    | −0.309        | 1.142    | −0.099        | 0.711    | −0.439        |
| 0.450  | 1.091    | 1.211    | 0.110         | 0.724    | −0.336        | 0.984    | −0.098        | 0.588    | −0.461        |
| 0.500  | 0.953    | 1.049    | 0.101         | 0.494    | −0.482        | 0.853    | −0.105        | 0.401    | −0.579        |
| 0.550  | 0.832    | 0.936    | 0.125         | 0.405    | −0.513        | 0.760    | −0.086        | 0.329    | −0.605        |
| 0.600  | 0.729    | 0.792    | 0.086         | 0.217    | −0.703        | 0.643    | −0.117        | 0.176    | −0.758        |
| 0.650  | 0.639    | 0.715    | 0.119         | 0.154    | −0.758        | 0.581    | −0.091        | 0.125    | −0.804        |
| 0.700  | 0.564    | 0.607    | 0.077         | 0.086    | −0.848        | 0.493    | −0.125        | 0.070    | −0.876        |
| 0.750  | 0.495    | 0.558    | 0.128         | 0.071    | −0.856        | 0.454    | −0.083        | 0.058    | −0.883        |
| 0.800  | 0.433    | 0.472    | 0.090         | 0.032    | −0.926        | 0.383    | −0.115        | 0.026    | −0.940        |
| 0.850  | 0.379    | 0.446    | 0.176         | 0.022    | −0.941        | 0.362    | −0.045        | 0.018    | −0.952        |
| 0.900  | 0.329    | 0.373    | 0.133         | 0.012    | −0.964        | 0.303    | −0.079        | 0.010    | −0.970        |
| 0.950  | 0.284    | 0.296    | 0.043         | 0.002    | −0.994        | 0.241    | −0.152        | 0.001    | −0.995        |
| 1.000  | 0.244    | 0.237    | −0.028        | 0.000    | −0.998        | 0.193    | −0.210        | 0.000    | −0.999        |

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Table 3: Self Diffusion Coefficient of the LJ fluid, $T^* = 1.3$, $\Omega^{(1,1)} = 0.8836$

| $\rho$  | $D_{MD}$ | $D_{CC}$ | $r_{CC}$ | $D_{CE}$ | $r_{CE}$ | $D_{HC}$ | $r_{HC}$ | $D_{HS}$ | $r_{HS}$ |
|--------|----------|----------|----------|----------|----------|----------|----------|----------|----------|
| 0.025  | 7.462    | 7.515    | 0.007    | 7.473    | 0.001    | 9.566    | 0.282    | 9.512    | 0.275    |
| 0.050  | 3.684    | 3.726    | 0.011    | 3.678    | 0.002    | 4.744    | 0.288    | 4.683    | 0.271    |
| 0.075  | 2.449    | 2.449    | 0.000    | 2.409    | 0.016    | 3.118    | 0.273    | 3.067    | 0.252    |
| 0.100  | 1.843    | 1.818    | 0.014    | 1.774    | 0.037    | 2.314    | 0.256    | 2.258    | 0.252    |
| 0.150  | 1.229    | 1.182    | 0.039    | 1.139    | 0.074    | 1.504    | 0.224    | 1.450    | 0.179    |
| 0.200  | 0.924    | 0.855    | 0.074    | 0.802    | 0.132    | 1.089    | 0.178    | 1.021    | 0.105    |
| 0.450  | 0.353    | 0.307    | 0.130    | 0.246    | 0.302    | 0.391    | 0.107    | 0.314    | 0.111    |
| 0.500  | 0.299    | 0.260    | 0.131    | 0.203    | 0.322    | 0.331    | 0.106    | 0.258    | 0.137    |
| 0.550  | 0.254    | 0.216    | 0.151    | 0.159    | 0.373    | 0.275    | 0.081    | 0.203    | 0.202    |
| 0.600  | 0.212    | 0.191    | 0.100    | 0.136    | 0.359    | 0.243    | 0.146    | 0.172    | 0.184    |
| 0.650  | 0.178    | 0.159    | 0.106    | 0.105    | 0.407    | 0.203    | 0.139    | 0.134    | 0.246    |
| 0.700  | 0.145    | 0.128    | 0.119    | 0.076    | 0.478    | 0.163    | 0.121    | 0.096    | 0.335    |
| 0.750  | 0.117    | 0.100    | 0.147    | 0.053    | 0.549    | 0.127    | 0.086    | 0.067    | 0.425    |
| 0.800  | 0.094    | 0.075    | 0.204    | 0.035    | 0.631    | 0.095    | 0.013    | 0.044    | 0.530    |
| 0.850  | 0.073    | 0.059    | 0.197    | 0.024    | 0.677    | 0.075    | 0.022    | 0.030    | 0.589    |
| 0.900  | 0.055    | 0.035    | 0.362    | 0.011    | 0.795    | 0.045    | 0.187    | 0.014    | 0.739    |
| 0.950  | 0.040    | 0.033    | 0.184    | 0.009    | 0.766    | 0.042    | 0.039    | 0.012    | 0.702    |
Table 4: **Self Diffusion Coefficient of the LJ fluid, \( T^* = 1.0, \Omega^{(1,1)} = 1.439 \)**

| \( \rho \) | \( D_{MD} \) | \( D_{CC} \) | \( r_{CC} \) | \( D_{CE} \) | \( r_{CE} \) | \( D_{HC} \) | \( r_{HC} \) | \( D_{HS} \) | \( r_{HS} \) |
|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| 0.005 | 29.427 | 29.354 | -0.002 | 29.328 | -0.003 | 42.241 | 0.435 | 42.202 | 0.434 |
| 0.010 | 14.547 | 14.649 | 0.007 | 14.627 | 0.005 | 21.080 | 0.449 | 21.048 | 0.447 |
| 0.015 | 9.595 | 9.744 | 0.016 | 9.718 | 0.013 | 14.022 | 0.461 | 13.985 | 0.458 |
| 0.020 | 7.203 | 7.290 | 0.012 | 7.267 | 0.009 | 10.490 | 0.456 | 10.457 | 0.452 |
| 0.025 | 5.710 | 5.825 | 0.020 | 5.797 | 0.015 | 8.382 | 0.468 | 8.342 | 0.461 |
| 0.030 | 4.770 | 4.842 | 0.015 | 4.818 | 0.010 | 6.967 | 0.461 | 6.933 | 0.453 |
| 0.035 | 4.040 | 4.140 | 0.025 | 4.113 | 0.018 | 5.957 | 0.475 | 5.919 | 0.465 |
| 0.040 | 3.529 | 3.613 | 0.024 | 3.584 | 0.016 | 5.200 | 0.473 | 5.158 | 0.461 |
| 0.045 | 3.131 | 3.210 | 0.025 | 3.183 | 0.016 | 4.619 | 0.475 | 4.580 | 0.463 |
| 0.050 | 2.813 | 2.876 | 0.022 | 2.849 | 0.013 | 4.138 | 0.471 | 4.100 | 0.457 |
| 0.055 | 2.544 | 2.608 | 0.025 | 2.579 | 0.014 | 3.752 | 0.475 | 3.711 | 0.459 |
| 0.060 | 2.348 | 2.392 | 0.019 | 2.363 | 0.006 | 3.443 | 0.466 | 3.400 | 0.448 |
| 0.065 | 2.169 | 2.198 | 0.014 | 2.168 | -0.001 | 3.163 | 0.458 | 3.119 | 0.438 |
| 0.070 | 2.014 | 2.033 | 0.010 | 2.002 | -0.006 | 2.926 | 0.453 | 2.881 | 0.431 |
| 0.075 | 1.897 | 1.919 | -0.014 | 1.899 | -0.011 | 2.807 | 0.447 | 2.766 | 0.429 |
| 0.080 | 1.790 | 1.804 | -0.017 | 1.794 | -0.013 | 2.650 | 0.440 | 2.610 | 0.426 |
| 0.085 | 1.687 | 1.702 | -0.017 | 1.690 | -0.015 | 2.485 | 0.434 | 2.448 | 0.423 |
| 0.090 | 1.589 | 1.605 | -0.017 | 1.592 | -0.016 | 2.315 | 0.429 | 2.280 | 0.421 |

Table 5: **Self Diffusion Coefficient of the LJ fluid, \( T^* = 0.8, \Omega^{(1,1)} = 1.612 \)**

| \( \rho \) | \( D_{MD} \) | \( D_{CC} \) | \( r_{CC} \) | \( D_{CE} \) | \( r_{CE} \) | \( D_{HC} \) | \( r_{HC} \) | \( D_{HS} \) | \( r_{HS} \) |
|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| 0.005 | 23.331 | 23.436 | 0.004 | 23.415 | 0.004 | 37.778 | 0.619 | 37.744 | 0.618 |
| 0.010 | 11.455 | 11.692 | 0.021 | 11.676 | 0.019 | 18.847 | 0.645 | 18.822 | 0.643 |
| 0.015 | 7.589 | 7.780 | 0.025 | 7.759 | 0.022 | 12.542 | 0.653 | 12.508 | 0.648 |
| 0.020 | 5.646 | 5.817 | 0.030 | 5.797 | 0.027 | 9.378 | 0.661 | 9.345 | 0.655 |
| 0.025 | 4.460 | 4.644 | 0.041 | 4.622 | 0.036 | 7.486 | 0.679 | 7.450 | 0.671 |
| 0.030 | 3.709 | 3.862 | 0.041 | 3.841 | 0.036 | 6.225 | 0.678 | 6.192 | 0.670 |
| 0.035 | 3.088 | 3.207 | 0.045 | 3.262 | 0.040 | 5.261 | 0.677 | 5.238 | 0.668 |
| 0.040 | 2.537 | 2.656 | 0.049 | 2.631 | 0.044 | 4.545 | 0.676 | 4.523 | 0.667 |
| 0.045 | 2.067 | 2.186 | 0.053 | 2.173 | 0.048 | 3.985 | 0.675 | 3.965 | 0.666 |
| 0.050 | 1.677 | 1.805 | 0.057 | 1.796 | 0.052 | 3.585 | 0.674 | 3.568 | 0.665 |
| 0.055 | 1.367 | 1.494 | 0.062 | 1.501 | 0.056 | 3.295 | 0.673 | 3.280 | 0.664 |
| 0.060 | 1.137 | 1.264 | 0.067 | 1.259 | 0.060 | 2.955 | 0.672 | 2.945 | 0.663 |
| 0.065 | 0.987 | 1.114 | 0.072 | 1.140 | 0.064 | 2.575 | 0.671 | 2.567 | 0.662 |
| 0.070 | 0.828 | 0.914 | 0.077 | 0.902 | 0.068 | 2.185 | 0.671 | 2.178 | 0.661 |


Table 6: **Self Diffusion Coefficient of the LJ fluid, \( T^* = 0.7 \), \( \Omega^{(1,1)} = 1.729 \)

| \( \rho \)   | \( D_{MD} \) | \( D_{CC} \) | \( r_{CC} \) | \( D_{CE} \) | \( r_{CE} \) | \( D_{HC} \) | \( r_{HC} \) | \( D_{HS} \) | \( r_{HS} \) |
|------------|-------------|-------------|-------------|-------------|-------------|-------------|-------------|-------------|-------------|
| 0.005      | 20.223      | 20.433      | 0.010       | 20.418      | 0.010       | 35.329      | 0.747       | 35.303      | 0.746       |
| 0.010      | 9.979       | 10.194      | 0.022       | 10.179      | 0.020       | 17.625      | 0.766       | 17.599      | 0.764       |
| 0.015      | 6.562       | 6.785       | 0.034       | 6.768       | 0.031       | 11.732      | 0.788       | 11.702      | 0.783       |
| 0.750      | 0.058       | 0.042       | -0.275      | 0.040       | -0.311      | 0.073       | 0.253       | 0.069       | 0.191       |
| 0.800      | 0.043       | 0.029       | -0.322      | 0.029       | -0.321      | 0.050       | 0.173       | 0.050       | 0.174       |
| 0.850      | 0.030       | 0.015       | -0.494      | 0.016       | -0.474      | 0.026       | -0.125      | 0.027       | -0.090      |

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