CONVERGENCE AND CONCENTRATION DEPENDENCE OF ISOTOPIC THERMAL DIFFUSION FACTOR

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SUMMARY — The convergence and the concentration dependence of the isotopic thermal diffusion factor is theoretically studied, on the basis of Lennard-Jones and exponential-six models.

The concentration dependence is not negligible *a priori* for binary mixtures of light isotopes, and significant differences may be expected for α_T if one or other of the isotopes is present in tracer concentrations.

In the majority of practical cases, the Kihara-Mason scheme of approximation provides better convergence and is therefore preferred.

1 — INTRODUCTION

According to the theory of Chapman and Enskog for non-uniform gases (1, 2), the expressions for transport coefficients are obtained from solutions to infinite set of simultaneous equations.

Two alternative schemes of series solutions have been proposed, one by Chapman & Cowling (1) and the other by Kihara (3) which has been extended by Mason (4).

The convergence of the series, in both schemes, is dependent on the particular form of the intermolecular potential assumed, but it is known to be fast for viscosity, thermal conductivity and concentration diffusion.

For thermal diffusion the convergence is comparatively slower and the differences between the values corresponding to the same order of approximation in both schemes may be quite significant. The potential form, the temperature, the mass and the concentration of the molecules are of much more influence on the convergence than in the other transport phenomena.

Furthermore, the complexity of the mathematical expressions for thermal diffusion increases tremendously for higher order of approximations, which makes theoretical studies very involvent and only possible by numerical means.

For those reasons, the convergence is mostly studied by considering mixtures having extreme cases of mass and/or concentration ratios, like Lorentzian, Masonian and isotopic mixtures (5), which may bracket most real mixtures.

For real binary mixtures with «normal» behaviour in the sense that the thermal diffusion factor, α_T, does not change sign with concentration, one may take the advantage of the discovery of one of us (6, 7, 8) that the inverse of α_T is approximately linear with concentrations (9, 10). The importance of this result is that it can reduce the magnitude of the convergence problem to the limiting cases corresponding to the mole fractions of the components equal to unity (5).

In this paper we consider the convergence of the theoretical approximations to the isotopic thermal diffusion factor as given by Chapman-Cowling and Kihara-Mason schemes, on the basis of Lennard-Jones and exponential-six models which are of common use to fit experimental data.

Concentration dependence which is certainly significant for mixtures of light isotopes is also discussed.

2 — THEORETICAL FORMULAS

For a binary mixture of isotopes, the thermal diffusion factor can be written in the following form:

$$\alpha_T = \alpha_0 M_{12} [1 + \gamma (x_1 - x_2) M_{12} + \ldots]$$

$$M_{12} = \frac{m_1 - m_2}{m_1 + m_2} \quad ; \quad x_1 + x_2 = 1 \qquad [1]$$

where m_1, m_2 and x_1, x_2 are, respectivelly, the molecular masses and the mole fractions of isotopes of kind 1 and 2.

α_0 — the so called reduced isotopic thermal diffusion factor — and γ are dimensionless quantities depending only on the temperature and the particular model considered. For the Chapman-Cowling scheme of solution (1, 2, 5), γ is given by

$$[\gamma]^{C} = \frac{3\,(5 - A^{\star})}{2\,(5 + 2\,A^{\star})} - \frac{5 - 3\,(5 - 4\,B^{\star})/5}{(5 + 2\,A^{\star}) + 3\,(5 - 4\,B^{\star})/8} \qquad [2]$$

and the first approximation to the reduced isotopic thermal diffusion factor, which we denote by $[\alpha_0]_1^C$, is given by

$$[\alpha_0]_1^{C} = \frac{15\,(6\,C^{\star} - 5)}{16\,A^{\star}} \cdot \frac{5 + 2\,A^{\star}}{5 + 2\,A^{\star} + (5 - 4\,B^{\star})/8} \qquad [3]$$

where $A^{\star}, B^{\star}$ and $C^{\star}$ have their usual meaning.

The Kihara-Mason expressions for γ and for the first approximation of the reduced isotopic thermal diffusion factor, $[\alpha_0]_1^K$, can be obtained from equations [2] and [3], by dropping the factors $(5 - 4\,B^{\star})$:

$$[\gamma]^{K} = \frac{5 - 3\,A^{\star}}{2\,(5 + 2\,A^{\star})} \quad ; \quad [\alpha_0]_1^{K} = \frac{15\,(6\,C^{\star} - 5)}{16\,A^{\star}} \qquad [4]$$

Expressions for the reduced isotopic thermal diffusion factor in both schemes have been calculated as far as the second approximation only (4) which are expected to be accurate within 1 % (11).

Since they are very complex, we do not give them here.

Equation [1] to the isotopic thermal diffusion factor, α_T, is a series development of a general expression, and is valid when molecular masses m_1 and m_2 are close enough, and the potential parameters are assumed to be equal for both isotopes.

With such hypotheses, convergence studies of α_T have to consider, at least in principle, the convergence of successive approximations for α_0 according to Chapman-Cowling and Kihara-Mason schemes and, on the other hand, the influence of the series development in equation [1] which involves γ and the concentration dependence.

Both cases will be considered separately in this paper.

3 — REMARKS ON CONCENTRATION DEPENDENCE

The concentration-dependent term involving γ in equation [1] has always been neglected in experiments, even in the case of light isotopic mixtures like ${}^3He - {}^4He$ (12, 13, 14, 15).

However, the increasing accuracy of the experimental determinations of α_T justifies some considerations on the magnitude of that term.

In the extreme case of the rigid elastic sphere model, the Chapman and Kihara values of γ are obtained from equations [2] and [4], respectively, by making into them $A^* = B^* = 1$. We have then

$$[\gamma]^C (r.\ e.\ s.) = 538/2065 = 0.2605$$

$$[\gamma]^K (r.\ e.\ s.) = 1/7 = 0.1429$$

For more realistic models the values of $[\gamma]^K$ and $[\gamma]^C$ are somewhat smaller and not so markedly different, having a small temperature dependence. They can be correlated by the equation

$$[\gamma]^C = [\gamma]^K + (5 - 4\,B^*) \,.\, \frac{3/5 + 15/8\,(5 + 2\,A^*)}{5 + 2\,A^* + 3(5 - 4\,B^*)/8}$$

where the coefficient of $(5 - 4\,B^*)$ is of the order of 1/8 to 1/9.

For lower reduced temperatures, let us say for $T^* < 1$ in the cases of the Lennard-Jones and the exponential-six models, B^* may be somewhat bigger than 5/4. Therefore $[\gamma]^C$ is somewhat smaller than $[\gamma]^K$.

In the majority of the practical cases, $5 - 4\,B^*$ is in between zero and unity. Therefore, $[\gamma]^C > [\gamma]^K$, and the Chapman-Cowling scheme of approximation will predict a somewhat larger concentration dependence for α_T.

Bearing in mind the above considerations, it follows that the concentration-dependent term may not be negligible, *a priori*, in the equation [1] for the isotopic thermal diffusion factor, and the ratio $[\alpha_T]_{x_1=1}/[\alpha_T]_{x_2=1}$ may be significant in the case of accurate experimental determinations, if the mass coefficient M_{12} is not sufficiently small.

Equation [1] predicts a linear dependence of the isotopic thermal diffusion factor with concentrations. This should be regarded as an approximation which is not in practical contradiction with the more general linear dependence of $1/\alpha_T$, once assumed that the quantity $\gamma\, M_{12}$ is small in comparison with unity.

4 — CONVERGENCE OF THE REDUCED ISOTOPIC THERMAL DIFFUSION FACTOR

Due to increasing computation facilities, a number of numerical tables have been prepared in recent years for several intermolecular potential models.

The present situation for the Lennard-Jones and the exponential-six models, which are in common use for interpretation of thermal diffusion, is presented in table I, with the references of the tabulated values for the different approximations of α_0. The general potential equations for those models are, respectively,

TABLE I

References for tabulations of α_0 approximations

Approx. / Models	Kihara - Mason		Chapman - Cowling	
	$[\alpha_0]_1^K$	$[\alpha_0]_2^K$	$[\alpha_0]_1^C$	$[\alpha_0]_2^C$
Lennard-Jones:				
9–6	This work	16	This work	·
12–6	This work	19, 20	21	·
28–7	This work	16	This work	·
Exp. - six:				
$\alpha = 12$	17, 18	21	17, 18	19
$\alpha = 13$	This work	21	This work	19
$\alpha = 14$	This work	21	This work	19
$\alpha = 15$	17, 18	21	17, 18	19
$\alpha = 16$	19	·	·	·
$\alpha = 17$	19	·	·	·

$$\varphi(r) = \frac{m\,\varepsilon}{m-n}\,(m/n)^{n/(m-n)}\left[(\sigma/r)^m - (\sigma/r)^n\right]$$

$$\varphi(r) = \frac{\varepsilon}{1-6/\alpha}\left\{\frac{6}{\alpha}\exp\left[\alpha\left(1 - r/r_m\right)\right] - (r_m/r)^6\right\}$$

where the letters have their usual meaning.

For the Lennard-Jones model we consider the cases where the pair of parameters (m, n) is equal to (12,6), which is the most frequently used, and also the pairs (9,6) and (28,7) recently studied (16).

For the exponential-six model we consider the usual range of the parameter α, from 12 to 17.

To study the convergence of α_0, we have computed several first approximations which are presented in tables II and III.

TABLE II

Reduced isotopic thermal diffusion factor for Lennard-Jones models

Reduced Temp. T^*	9-6		12-6	28-7	
	$[\alpha_0]_1^K$	$[\alpha_0]_1^C$	$[\alpha_0]_1^K$	$[\alpha_0]_1^K$	$[\alpha_0]_1^C$
0.10	0.261	0.259	...	0.384	0.377
0.15	0.209	0.209	...	0.386	0.379
0.20	0.131	0.132	...	0.385	0.378
0.30	− 0.024	− 0.024	0.075	0.366	0.360
0.40	− 0.123	− 0.125	0.002	0.336	0.332
0.50	− 0.169	− 0.171	− 0.042	0.310	0.307
0.60	− 0.179	− 0.180	− 0.056	0.296	0.293
0.70	− 0.178	− 0.179	− 0.051	0.291	0.287
0.80	− 0.158	− 0.157	− 0.035	0.295	0.290
0.90	− 0.125	− 0.124	− 0.009	0.304	0.299
1.00	− 0.090	− 0.089	0.017	0.318	0.312
1.50	0.058	0.057	0.154	0.402	0.390
2.0	0.185	0.181	0.262	0.480	0.464
3.0	0.326	0.317	0.398	0.577	0.555
4.0	0.395	0.384	0.466	0.633	0.608
5.0	0.437	0.424	0.503	0.665	0.638
6.0	0.462	0.449	0.531	0.685	0.658
7.0	0.477	0.464	0.543	0.698	0.670
8.0	0.487	0.473	0.555	0.708	0.680
9.0	0.494	0.480	0.558	0.716	0.687
10.0	0.498	0.484	0.566	0.722	0.692
15.0	0.508	0.493	....	0.737	0.707
20.0	0.509	0.495	0.574	0.743	0.712
30.0	0.507	0.493	0.575	0.748	0.717
40.0	0.503	0.489	0.574	0.749	0.718
50.0	0.500	0.487	0.572	0.750	0.720
60.0	0.497	0.484	0.571	0.751	0.720
70.0	0.495	0.482	0.570	0.751	0.720
80.0	0.493	0.480	0.570	0.752	0.721
90.0	0.491	0.478	0.569	0.751	0.721
100.0	0.490	0.477	0.568	0.752	0.721

TABLE III

Reduced isotopic thermal diffusion factor for exp. - 6 models

Reduced Temp. T^*	$\alpha = 13$		$\alpha = 14$	
	$[\alpha_0]_1^K$	$[\alpha_0]_1^C$	$[\alpha_0]_1^K$	$[\alpha_0]_1^C$
0.1	0.283	0.280	0.285	0.282
0.2	0.218	0.218	0.233	0.232
0.3	0.104	0.105	0.130	0.131
0.4	0.014	0.014	0.045	0.046
0.5	− 0.039	− 0.039	− 0.004	− 0.004
0.6	− 0.061	− 0.062	− 0.025	− 0.026
0.7	− 0.063	− 0.063	− 0.027	− 0.027
0.8	− 0.052	− 0.051	− 0.016	− 0.016
0.9	− 0.033	− 0.032	0.002	0.002
1.0	− 0.009	− 0.010	0.025	0.025
1.2	0.043	0.043	0.076	0.074
1.4	0.095	0.094	0.127	0.124
1.6	0.143	0.140	0.174	0.170
1.8	0.186	0.182	0.215	0.210
2.0	0.223	0.218	0.251	0.244
2.5	0.295	0.287	0.321	0.313
3.0	0.346	0.336	0.371	0.361
3.5	0.382	0.372	0.407	0.395
4.0	0.408	0.397	0.433	0.420
5.0	0.442	0.430	0.465	0.452
6.0	0.461	0.448	0.487	0.473
7.0	0.472	0.459	0.498	0.484
8.0	0.478	0.466	0.506	0.491
9.0	0.481	0.468	0.509	0.495
10.0	0.482	0.470	0.511	0.497
12.0	0.482	0.470	0.513	0.499
14.0	0.481	0.469	0.512	0.498
16.0	0.478	0.466	0.510	0.496
18.0	0.476	0.464	0.508	0.494
20.0	0.472	0.460	0.507	0.494
25.0	0.465	0.454	0.503	0.489
30.0	0.461	0.450	0.499	0.486
35.0	0.457	0.446	0.496	0.483
40.0	0.455	0.444	0.495	0.482
45.0	0.454	0.442	0.494	0.480
50.0	0.452	0.440	0.493	0.480
60.0	0.450	0.438	0.493	0.479
70.0	0.446	0.434	0.495	0.481
80.0	0.448	0.437	0.497	0.483
90.0	0.448	0.437	0.499	0.485
100.0	0.449	0.438	0.500	0.486
200.0	0.460	0.447	0.518	0.502

As table I shows, the second Kihara-Mason approximation to the reduced thermal diffusion factor, $[\alpha_0]_2^K$, has been tabulated for the majority of the models. For that reason, it will be regarded as a reference in our global considerations about convergence which will be studied by means of the ratio

$$\alpha_0 / [\alpha_0]_2^K$$

where α_0 denotes, in general, the first Kihara approximation, $[\alpha_0]_1^K$, and the first and second Chapman approximations, $[\alpha_0]_1^C$ and $[\alpha_0]_2^C$, respectively.

The three ratios defined in the above way show a similar behaviour with the reduced temperature, T^*, for all the special cases studied, what simplifies appreciably the discussion on the convergence of α_0.

In fig. 1 we present the tipical cases for Lennard-Jones (12,6) and exponential-six ($\alpha = 14$) models.

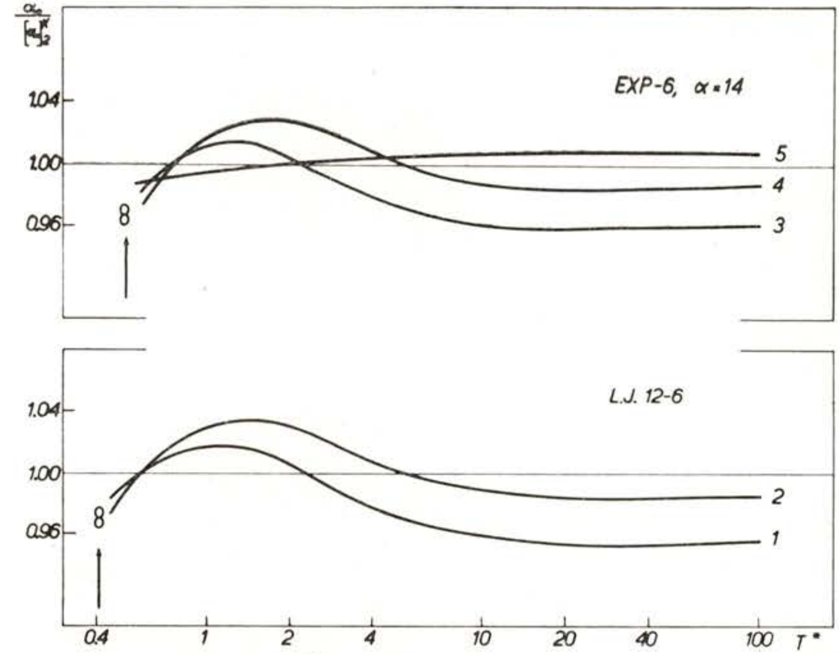

Fig. 1 — Ratios $\alpha_0 / [\alpha_0]_2^K$ against reduced temperature, for Lennard-Jones (12, 6) and exponential-six ($\alpha = 14$) models.

Curves 1 and 3 — σ_0 equals to $[\alpha_0]_1^C$ (CHAPMAN)
Curves 2 and 4 — α_0 equals to $[\sigma_0]_1^K$ (KIHARA)
Curve 5 — σ_0 equals to $[\sigma_0]_2^C$ (CHAPMAN)

The arrow localizes the value of T^* for which $[\alpha_0]_2^K = 0$.

Unfortunately, $[\alpha_0]_2^C$ has not been tabulated for that important case of the Lennard-Jones model because several collision integrals, $\Omega^{(l,s)\star}$, which are needed, have not been computed yet for higher values of (l, s). However, it may be expected that the general trend of $[\alpha_0]_2^C/[\alpha_0]_2^K$ may be similar to the corresponding ratios for the exponential-six models, i. e., a trend similar to the curve 5 in fig. 1.

By taking fig. 1 as representative of a general behaviour, we may conclude the following:

a) Kihara and Chapman second approximations agree within about $\pm 1\,\%$ (see curve 5).

b) For higher reduced temperatures, say for $T^\star > 3$, the Kihara-Mason scheme provides faster convergence, and the difference between $[\alpha_0]_2^K$ and $[\alpha_0]_1^K$ is of the order of $2\,\%$ (see curves 2 and 4).

c) The situation is reserved for lower reduced temperatures, where the Chapman-Cowling scheme of approximations provides better convergence.

d) Except at lower temperatures, $[\alpha_0]_1^K > [\alpha_0]_1^C$. This conclusion is also inferred by comparison of equations [3] and [4], since usually $(5 - 4B^\star) > 0$.

The above discussion is limited to the temperature range $100 > T^\star > 0.4$ which covers the most common practical cases. For lower temperatures α_0 reverses sign for some potential models. Therefore the ratio $\alpha_0/[\alpha_0]_2^K$ is not adequated to study the convergence.

On the other hand, the conclusions may be extrapolated for $T^\star > 100$ since that ratio and the thermal diffusion factor as well remain almost constant.

5 — CONCLUSIONS

As we have done in this paper, theoretical study of the isotopic thermal diffusion factor seems to be conveniently divided into two aspects: *a*) one concerning the convergence of the reduced factor, α_0; *b*) the other referring to the concentration-dependent term involving the quantity γ in equation [1].

On the basis of the Lennard-Jones and the exponential-six intermolecular potentials which are in common use to fit experimental data, the Kihara-Mason scheme of approximations provides faster convergence for α_0, at higher reduced temperatures, say for $T^\star > 3$.

Other remarkable feature of this scheme is that theoretical formulas are simpler and involving a smaller number of collision integrals, therefore reducing appreciably a number of complex numerical computations.

Regarding the concentration dependence, it is certainly advisable to take it into account in accurate determinations of the thermal diffusion factor for mixtures of light isotopes, specially if one of them is present in tracer concentrations only.

In the majority of practical cases, say for $T^* > 1$, the Chapman-Cowling scheme gives rize to somewhat higher concentration dependence, since $[\gamma]^C > [\gamma]^K$ in equation [1].

Of course, we may not say, on theoretical bases only, that such dependence will be in better accordance with experiments, but we might expect it since this is the usual behaviour for non-isotopic mixtures. However, this aspect may hardly be detected in practice, for isotopic mixtures.

As an over-all conclusion, we may say that each scheme of approximation has its own theoretical advantages and limitations, but in the majority of practical cases of isotopic thermal diffusion the Kihara-Mason scheme is preferred.

Recently, PAUL, HOWARD & WATSON (10) carried out accurate experiments with $^3He - {}^4He$ mixtures which provide a significant example for comparison with the theory. This will be done in a following paper.

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