Master equation modelling of nonequilibrium chemistry in stellar outflows II. Accounting for detailed balance.

Article:

Green, N. J. B., Plane, J. M. C. orcid.org/0000-0003-3648-6893 and Robertson, S. H. (2025) Master equation modelling of nonequilibrium chemistry in stellar outflows II. Accounting for detailed balance. Chemical Physics Letters, 865. 141943. ISSN 0009-2614

https://doi.org/10.1016/j.cplett.2025.141943

Master equation modelling of nonequilibrium chemistry in stellar outflows II. Accounting for Detailed Balance.

Nicholas J. B. Green[a], John M. C. Plane[b] and Struan H. Robertson[c,*]

[a]Inorganic Chemistry Laboratory, University of Oxford, South Parks Road, Oxford OX1 3QR, UK

[b]School of Chemistry, University of Leeds, Woodhouse Lane, Leeds LS2 9JT, UK

[c]Dassault Systèmes, Cambridge Science Park, Cambridge, CB4 0FJ, UK

*Corresponding author: Email address, struanhrobertson@gmail.com

Keywords: ISM, association, reaction, detailed-balance,

Abstract

Technical issues in respect of the observance of detailed balance in the calculation of rate coefficients in the circumstellar environment are discussed. The central problem is that of two competing heat baths that are at different temperatures (vibrational disequilibrium), and it is not immediately clear as to how detailed balance should be applied. This issue is discussed and a possible approach to the problem presented.

Introduction

In a recent article [1] the problem of silicate formation in the outflow from an oxygen-rich AGB star was discussed. Fe–Mg silicate dust is observed to form between two and three stellar radii from these stars. The discussion focused on one reaction in particular, that of water with silicon dioxide to form meta-silicic acid:

$$\mathrm{H_2O + SiO_2 \rightleftarrows\ H_2SiO_3} \tag{1}$$

This association reaction is thought to be one of the first steps in formation of silicates. As discussed in [1] the prevailing conditions in the ISM at two stellar radii from the star are such that the collision temperature is of the order of 1500 K and at this temperature the equilibrium for reaction (1) lies strongly in favour of the reactants. A further complication is that in the gas phase the nascent adduct must be stabilized or it will simply fall apart again. A recombination reaction such as (1) is normally facilitated by stabilization through collision with a bath gas present in excess. In the ISM the concentration of bath gas (H_2) is very low (< 0.1 Pa). This has the consequence that the formation of the adduct, even if equilibrium was favourable, will be very slow. Given this, the question arises how could silicic acid be formed under these conditions?

In Ref. [1] a possible mechanism was advanced in which coupling to the electromagnetic field may represent an alternative stabilization mechanism, that is the presence of a radiation field and low gas densities leads to a situation whereby cooling can take place leading to the adducts being formed that might not otherwise exist. For this mechanism to work the radiation field at two stellar radii must be at an apparent temperature significantly lower than that of the thermal collision temperature. It was shown that this mechanism can lead to the stabilization of the adduct, a process referred to as optical cooling, leading to the formation of $\mathrm{H_2SiO_3}$.

The purpose of this note is to present some of the underlying technical difficulties associated with the proposed mechanism, specifically those related to detailed balance, and show the approach taken to resolve them, allowing effective rate coefficients to be obtained.

Theory

As discussed in the introduction, the kinetic temperature at two stellar radii is around 1500 K and at this temperate the equilibrium of reaction (1) lies strongly in favour of the left-hand side, the dissociated state, and so it would appear that this cannot be a route to silicate formation. In Ref. [1] a possible solution to this difficulty was presented where the system was not only coupled to a collision (thermal) bath of 1500 K but also a radiation bath at a different temperature. In terrestrial experiments the impact of radiation is usually neglected as it is small relative to collision transitions, but at the concentrations of the bath gas in the ISM (typically 10^{11}molecules cm^{-3} at two stellar radii) the rates of optical transitions are comparable with rate of collisional transitions.

The apparent temperature of the radiation bath at approximately two stellar radii (one stellar radius from the surface of the star) was inferred from the vibrational energy and found to be 660 K, significantly different from that of the collision bath. It is also significantly different from the surface temperature of the star which is approximately 2500 K. The apparent radiation temperature emerged from master equation calculations, the details of which are described shortly. For now, it is sufficient to say that this value is consistent with the observations of Fonfría et al [2,3].

This difference in bath temperatures is a situation that is clearly not thermodynamically stable: in the long term both baths must eventually reach the same temperature (at maybe 100 stellar radii) through various mechanisms including adiabatic expansion and radiative emission. However, it appears to be a situation that persists for a sufficiently long time so that, to a first approximation, the baths can be regarded as being at separate temperatures. Adopting this approximation immediately provokes several questions connected with detailed balance: what temperature should be used in defining the detailed balance relations and what temperature should be used to define the equilibrium constant for the reaction (1)?

To attempt to address these questions a modified master equation (ME) model [4], as proposed in Ref. [1], was developed. Strictly speaking, reaction (1) would lead to a non-linear ME, which is difficult to solve and extract rate coefficients from. This difficulty can be addressed in several ways, for example by the methods developed by Klippenstein, Miller and co-workers [5]. Here, the approximation developed by Pilling and co-workers of assuming that one of the reactants, in the present case $\mathrm{H_2O}$, can be assumed to be in relative excess concentration will be adopted [4,6]. This approximation allows a collisional ME for reaction (1) to be written as follows:

$$\frac{\mathrm{d}}{\mathrm{dt}}\begin{pmatrix}\boldsymbol{\rho}\\ x_{\mathrm{SiO_2}}\end{pmatrix}=\begin{pmatrix}\boldsymbol{M}-\boldsymbol{K} & \boldsymbol{\varphi}\\ \boldsymbol{k} & -k_b[\mathrm{H_2O}]\end{pmatrix}\begin{pmatrix}\boldsymbol{\rho}\\ x_{\mathrm{SiO_2}}\end{pmatrix} \tag{2}$$

where $\boldsymbol{\rho}$ is the rovibrational distribution of $\mathrm{H_2SiO_3}$, $x_{\mathrm{SiO_2}}$ is the mole fraction of $\mathrm{SiO_2}$, $\boldsymbol{K}$ is a diagonal matrix of unimolecular microcanonical rate coefficients, $\boldsymbol{k}$ is a row vector of same, $[\mathrm{H_2O}]$ is the concentration of $\mathrm{H_2O}$, assumed to be in excess and $\boldsymbol{\varphi}$ is the partitioning of the forward flux derived from detailed balance. In previous work the matrix $\boldsymbol{M}$ represented the collision transition operator and was subject to detailed balance, but here a modification is made to give a radiation-collision transition operator:

$$\boldsymbol{M} = \omega(\beta_c, [G])[\boldsymbol{P}(\beta_c) - \boldsymbol{I}] + \boldsymbol{R}(\beta_r) \tag{3}$$

where $\beta_c = 1/kT_c$, T_c being the collision temperature, β_r is the corresponding quantity for the radiation transitions and $[G]$ is the concentration of the collision bath gas. The matrix $\boldsymbol{P}(\beta_c)$ contains the collisional transition probabilities, which are usually modelled using some form of empirical model such as the exponential down model, details of which have been discussed elsewhere [4]. The coefficient $\omega(\beta_c, [G])$ is the collision frequency. The matrix $\boldsymbol{R}(\beta_r)$ represents the optical transitions, which are determined by the Einstein $A_{ij}(\upsilon)$ and $B_{ij}(\upsilon)$ coefficients associated with each frequency, υ:

$$A_{ij}(\upsilon) = \frac{8\pi\upsilon^3}{c^2}\sigma_{int}\ ;\ B_{ij}(\upsilon) = \frac{c^2}{8\pi h\upsilon^3}A_{ij}(\upsilon) \tag{4}$$

At equilibrium (and in the absence of collision) these coefficients are related by the detailed balance expression,

$$B_{ij}\rho(\upsilon, \beta_r)b_j(\beta_r) = (B_{ji}\rho(\upsilon, \beta_r) + A_{ji})b_i(\beta_r) \tag{5}$$

where $\rho(\upsilon, \beta_r)$is the radiation density for the frequency υ and β_r and $b_i(\beta_r)$ is the Boltzmann distribution associated with the reciprocal temperature β_r. Finally, the overall transition matrix of the ME on the RHS of Eq. (2) must obey certain constraints: it must conserve mass and its elements must obey detailed balance. This latter constraint is exploited in the solution of the ME below.

The functional form of $\rho(\upsilon, \beta_r)$ that satisfies Eq. (5) is the Planck distribution. At the stellar surface where the temperature is of the order of 2500 K the IR radiation field can, to a good approximation, be assumed to be the Planck distribution. However, at a distance from the surface, while the ratio between the intensities of any two frequencies remains the same, the absolute intensity of the radiation field will decline, and simple geometrical arguments suggest that this decline should follow an inverse square model. It therefore follows that $\rho(\upsilon, \beta_r)$ at a significant distance from the surface cannot, strictly speaking, be a Planck distribution of 2500 K. In Ref. [1], the intensities of the radiation field for the vibrational frequencies of $\mathrm{H_2SiO_3}$ were inferred from the MARCS [7] model, by rescaling a Planck distribution of 2500 K to match the MARCS model and used directly in a master equation model. In the region where the collision relaxation process is very slow, Eq. (5) will determine the approximate equilibrium distribution, the reduced intensities driving the system to the apparent vibration temperature of 660 K.

In more general applications, detailed intensities may not be available; however, the detailed balance constraint that Eq. (5) imposes requires a Planck distribution. For a given frequency, the only other parameter of the Planck distribution is the temperature, but what temperature should be used? For the present example, the above discussion suggests that the stellar surface temperature cannot be used, but the attenuated intensity of each frequency, based on the stellar surface temperature, is available. Following along similar lines to the rescaling described above, the temperature of the Planck distribution is the one such that has intensities that match the attenuated 2500 K intensities as closely as possible. An exact match is not possible and in practice it was found that more weight needs to be given to the lower frequencies of the molecule being studied (in this case, H_2SiO_3).

Eq. (2) can be solved in several ways, but the method used here is to determine the eigenvalues of the operator of the overall matrix on the RHS of Eq. (2). Typically, a preparatory step in finding the eigenvalues is the symmetrisation of the matrix $\boldsymbol{M}$ by a Boltzmann distribution, a procedure that follows from detailed balance. However, it is at this point that the difficulties described above become apparent as it is seen that the operator $\boldsymbol{M}$ depends on two temperatures, so which Boltzmann distribution should be used? Furthermore, implicit in Eq. (2) is the equilibrium constant for the reaction but because of the two temperatures there are two values for this quantity; again, which one should be used?

To make progress it is proposed that there is an effective single temperature for the reaction. At the extremes of $[G]$ one or other mechanism will dominate and so the effective temperature is straightforward to define. For intermediate values of $[G]$ an alternative approach is needed. In the absence of reaction, the distribution of $\boldsymbol{\rho}$ will tend to a stationary state, $\boldsymbol{f}$, which is the non-trivial solution to the equation,

$$\boldsymbol{M}\boldsymbol{f} = [\omega(\beta_c, [G])[\boldsymbol{P}(\beta_c) - \boldsymbol{I}] + \boldsymbol{R}(\beta_r)]\boldsymbol{f} = \boldsymbol{0} \tag{6}$$

It is likely, and close to the limiting cases of $[G]$ almost certain, that $\boldsymbol{f}$ will be similar in form to a Boltzmann distribution. So, an initial guess at this distribution would be a Boltzmann distribution, $\boldsymbol{b}(\beta)$, of some, as yet unspecified temperature β. Inserting this initial guess into the RHS of Eq. (4) gives,

$$\boldsymbol{M}\boldsymbol{b}(\beta) = \boldsymbol{r} \tag{7}$$

where the vector $\boldsymbol{r}$, the residual, is a function of β (for fixed β_c, β_r and $[G]$). It follows that the optimal value of β is that which minimizes the magnitude of $\boldsymbol{r}$. This value of β is then the value used as the effective temperature in the remainder of a standard ME calculation.

Application

The above development was applied to the reaction system given by Eq. (1). The details of the model used are the same as in Ref. [1]. Table 1 lists the frequencies used to calculate the density of states for $\mathrm{H_2SiO_3}$ and the corresponding Einstein A coefficients. The Einstein B coefficients for stimulated emission were calculated from Eq. (4) and the corresponding absorption coefficients follow from Eq. (5). The frequencies were obtained from the Gaussian suite of programs [8] using the B3LYP/6-311+g(2d,p) level of theory. The rotational constants for all species were obtained from the equilibrium geometries. The two H-O-Si=O internal rotors were treated as independent hindered rotors. The bath gas was taken to be $\mathrm{H_2}$ (the most abundant species in the ISM). The collisional energy transfer probability was modelled as exponential down with average energy transferred in a deactivating collision, $\langle \Delta E \rangle_d(T)$, given by,

$$\langle \Delta E \rangle_d(T) = 200 \left(\frac{T}{300\ K}\right)^{0.25} \ \mathrm{cm^{-1}} \tag{8}$$

where T is the (effective) temperature. The radiation field, $\rho(\upsilon, \beta_r)$, was modelled using a Planck distribution. The microcanonical rate coefficients that appear in Eq. (2) are obtained using the inverse Laplace transformation method applied to the high-pressure association rate coefficient using an estimated based on long-range transition state theory [9]:

$$k_{rec,\infty} = 8.7 \times 10^{-10} \left(\frac{T}{1200}\right)^{1/6} \ \mathrm{cm^3 molecule^{-1} s^{-1}} \tag{9}$$

Mode Number	Frequency/cm^{-1}	Aij/s^{-1}
1	313.19	0.4.68
2	321.27	0.038
3	361.07	0.21
4	423.91	-
5	492.2	3.57
6	820.78	3.5
7	836.79	7.24
8	907.47	8.13
9	1019.81	5.75
10	1278.14	18.8
11	3859.43	243
12	3861.1	1.91

Table 1 Frequencies and Einstein A coefficients for $\mathrm{H_2SiO_3}$

For applying Eq. (7) a definition of the magnitude of $\boldsymbol{r}$ is required. Perhaps the most obvious candidate is the standard Euclidean norm:

$$\|\boldsymbol{r}\|_2 = \sqrt{r_1^2 + r_2^2 + \cdots + r_n^2} \tag{10}$$

An alternative magnitude definition, and one which is more suitable when dealing with probabilities, is the one-norm:

$$\|\boldsymbol{r}\|_1 = \sum_{i=1}^{n} |r_i| \tag{11}$$

The general structure of the vector $\boldsymbol{r}$ reflects the Boltzmann distribution and so those elements of the vector associated with lower energies will be the largest values. This has the consequence that the $\|\boldsymbol{r}\|_2$ magnitude tends to give these elements more weight, while the $\|\boldsymbol{r}\|_1$magnitude definition tends to weight the elements more evenly. Both these definitions were implemented within the MESMER 7.1 code and compared for reaction (1). It was found that there was in fact little obvious distinction between these definitions, but as the $\|\boldsymbol{r}\|_1$ gave a slightly smoother curve

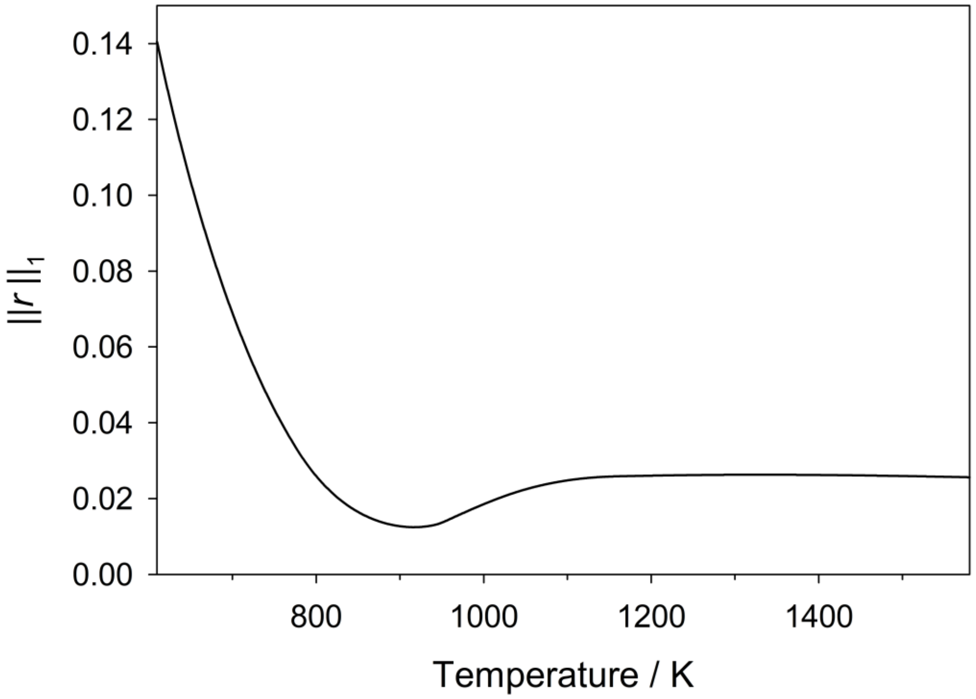

Fig.1 A plot of $\|\boldsymbol{r}\|_1$ as a function of temperature showing a minimum at 916 K

this was the definition adopted for all subsequent calculations. Figure 1 shows a plot of $\|\boldsymbol{r}\|_1$ against temperature for the conditions of a radiation field at 626 K, a collision temperature at 1583 K and a bath gas concentration of 10^{13} molecules cm^{-3}. A minimum is observed at 916 K and this is the effective temperature that is used for the determination of the rate coefficients for these conditions.

This algorithm was applied for a series of gas densities and the effective temperature of the adduct ($\mathrm{H_2SiO_3}$) as a function of the gas concentration is shown as the full red line in figure 2 (which is in the same format as figure 3a of Ref. [1]). There is an increase in the effective temperature (and therefore the internal energy) between bath gas concentrations of 10^{11} molecule cm^{-3} and 10^{15} molecules cm^{-3}. Also plotted on figure 2 are the rate coefficients for the dissociation of the adduct as the full black line. For comparison, the regular fall-off curve is plotted as the broken black line. As observed earlier, when the radiation field is present the rate coefficient declines in the same concentration interval as the change in internal energy, falling to the lower radiation limit. Comparison of figure 2 with figure 3a of Ref. [1] shows the same general shape but differences in implementation, particularly of the radiation temperature at two stellar radii, make a direct comparison difficult.

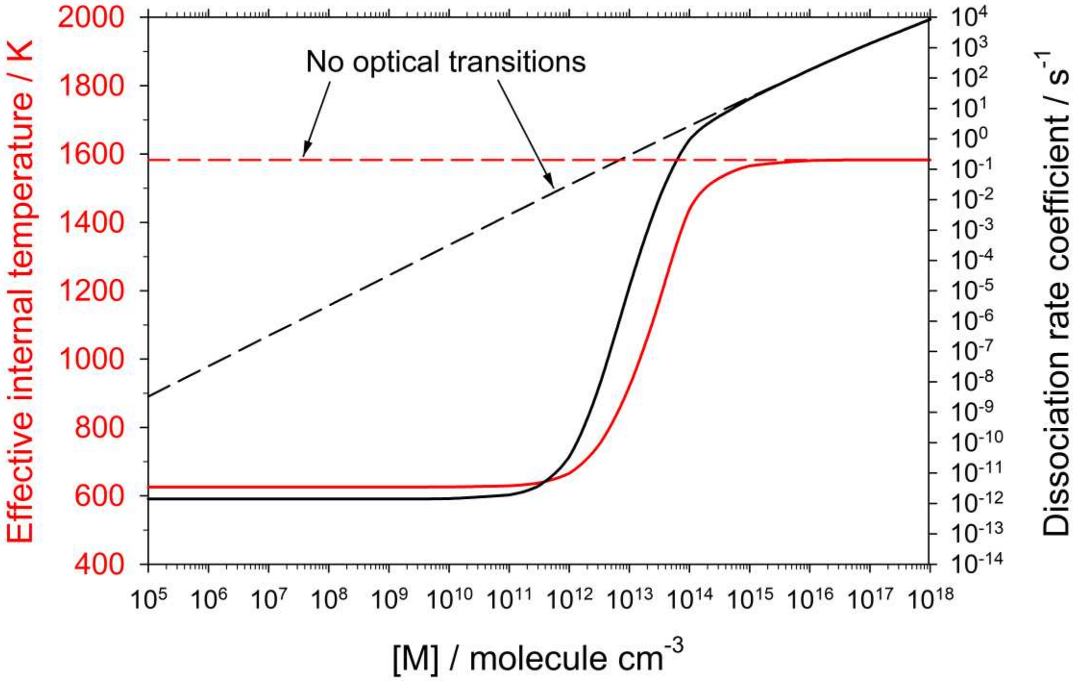

Fig.2 The effective temperature (full red line) and dissociation rate coefficient of reaction (1) as a function of bath gas concentration

Conclusion

In this note the technical issues regarding detailed balance in the ISM have been addressed. The difficulty that the ISM presents is that there appear to be two heat baths at different temperatures, one is the familiar collisional heat bath, the other is the heat bath due to a radiation field. This difference in temperatures poses a problem for standard master equation techniques as it is not clear which of these temperatures should be used to implement detailed balance. In this work the detailed balance issue has been addressed by finding an effective temperature for a given collision density. For the present example of reaction (1), this allows the effective adduct dissociation rate coefficient to be determined as a function of bath gas concentration. This dissociation rate coefficient is expected to decrease with bath gas concentration as a consequence of the usual fall-off mechanism, but it is observed that the decline in the rate coefficient is even more rapid for certain concentrations of bath gas. This rapid decline of the dissociation rate coefficient has the consequence that the equilibrium of reaction (1) is shifted in favour of the adduct and so is a possible first step to the production of silicates in the ISM.

In future work a wider range of conditions will be explored as well as other possible approaches to the problem of two temperature baths, such as the local detailed balance approach discussed by Maes [10].

Acknowledgements

The authors grateful to the University of Leeds for giving them access to the ARC facility on which the calculations described above were performed. JMCP was funded by UKRI STFC grant ST/T000287/1.

References

[1] J. M. C. Plane and S. H. Robertson, Faraday Discussions, 238 (2022) 461.

[2] J. P. Fonfría, E. J. Montiel, J. Cernicharo, C. N. DeWitt, M. J. Richter, J. H. Lacy, T. K. Greathouse, M. Santander-Garcia, M. Agundez and S. Massalkhi, *Astron. Astrophys.*, 651 (2021) art. no.: A8.

[3] J. P. Fonfría, J. Cernicharo, M. J. Richter and J. H. Lacy, *Astrophys. J.*, 673 (2008) 445.

[4] S. H. Robertson, Comprehensive Chemical Kinetics, 43 (2019) 299.

[5] J. A. Miller and S. J. Klippenstein, J. Chem. Phys. 110 (2006) 10528.

[6] M. A. Hanning-Lee, N. J. B. Green, M. J. Pilling and S. H. Robertson, J. Phys. Chem. 97 (1993) 860.

[7] B. Gustafsson, B. Edvardsson, K. Eriksson, U. G. Jørgensen, Å. Nordlund and B. Plez, A grid of MARCS model atmospheres for late-type stars, I. Methods and general properties, *Astron. Astrophys.*, 486 (2008) 951.

[8] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, N. R. J. Gao, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. J. A. Montgomery, J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman and D. J. Fox, Gaussian 16, Revision B.01, Gaussian, Inc., Wallingford, CT, USA, 2016.

[9] Y. Georgievskii and S. J. Klippenstein, J. Chem. Phys. 122 (2005) 194103.

[10] C.Maes, SciPost Phys. Lecture Notes 32 (2021).