Explicit Expression for the Relaxation Spectrum of a Model with Infinitely Many Coupled Chemical Reactions. II

OLE J. HEILMANN

Kemisk Laboratorium III, H.C. Ørsted Institutet, DK-2100 Copenhagen Ø, Denmark

Dedicated to Professor K. A. Jensen on his 70th birthday

In the first article of this series the explicit expression for the relaxation spectrum of the polymerization reaction $A_1 + A_n \rightleftharpoons A_{n+1}$ ($n = 1, 2, \dots$) was found under the assumption that all reactions had the same values of the thermodynamic and kinetic parameters. In the present article the method is generalized to allow the first reaction to deviate from the following reactions. The result does not show any surprising features compared to what would have been expected on the basis of the first article. But the new result is more directly applicable to actual experimental situations.

In the first article¹ (hereafter referred to as I) of this series the following reaction scheme for formation of polymers was considered:

An exact expression for the relaxation spectrum was found under the assumption that all the reactions behaved identically; i.e. that the reactions have identical values of the thermodynamic and kinetic parameters. In the present article the result is generalized to cover the case where the first reaction is allowed to be different.

In principle, the method can be generalized to cover the case where the m first reactions deviate from the remaining reactions. But the computations become extremely tedious in the general case, and the resulting expressions are so complicated that they will probably be of very limited value. Also, the present generalization is sufficient to cover several models suggested by experimentalists as realistic models for actual physical systems.

We assume the following reaction scheme (eqns. 2, 3).

If $\nu_0 = 0$ and $n \geq 2$ we have a polymerization which starts by the formation of an n -mer; if $n = 2$ we have the same reaction scheme as in eqn. (1) (taking $A_m = C_m$), while the case where n is somewhat larger ($n \sim 10$) might be considered as a model for micelle formation (this particular model with all reactions in eqn. (3) behaving identically does not appear to have been used in interpreting experiments on micelle formation kinetics, but rather similar models are discussed for example by Zana *et al.*²).

The possibility, $\nu_0 = 1$, will occur for formation of clusters of the solvent molecules (A_1) around a solute molecule (B); an example would be the structuring of water molecules around dissolved alcohol molecules (see for example the review article by Blandamer and Waddington³ and the more recent article on ethanol-water mixtures by Bruun *et al.*⁴).

BASIC NOTATION

The notation will follow the notation of I and the reader is referred to this article (in particular its section II) for the meaning of the vectors $\mathbf{f}$ and $\mathbf{h}$, the matrix $\mathbf{A}$ and the reaction rates g_j^2 ($j = 1, n+1, n+2, \dots$).

Here we use k_1 for the forward and k_{-1} for the backward rate constant for the reaction (2), and k_+ for the forward and k_- for the backward rate constant for (3). The corresponding equilibrium constants are

$$K_1 = k_1/k_{-1} \quad (4)$$

and

$$K = k_+/k_- \quad (5)$$

$\mathbf{e}_j$ will denote the j 'th unit vector and $\mathbf{e}^{(i)}$ the vector (superscript T stands for transposing; vectors are supposed to be column vectors):

$$\mathbf{e}^{(1)T} = \{0, 1, 1, \dots\} \quad (6)$$

The vectors $\mathbf{f}$ and $\mathbf{h}$ can then be written

$$\mathbf{f} = f_1 \mathbf{e}_1 + f \mathbf{e}^{(1)} \quad (7)$$

$$\mathbf{h} = h_1 \mathbf{e}_1 + h \mathbf{e}^{(1)} \quad (8)$$

The mol fraction of B is denoted x_b ; x_1 stands for the mol fraction of A_1 and x_j ($j = n, n+1, \dots$) stands for the mol fraction of C_j . As in I we introduce the parameter ϕ :

$$\phi = Kx_1 \quad (9)$$

and find

$$x_j = x_n \phi^{j-n}, j = n, n+1, \dots \quad (10)$$

We choose the unit of time to make k_- equal to one and write

$$\kappa_1 = k_{-1}/k_- \quad (11)$$

The rate of reaction, g_1^2 , corresponding to the reaction in (2) is given by

$$g_1^2 = \kappa_1 x_n \quad (12a)$$

while the rate of reaction, g_{m+1}^2 , corresponding to the reaction in (3) is given by

$$g_{m+1}^2 = x_n \phi^{m-n+1} \quad (12b)$$

The matrix $\mathbf{A}$ is divided in two parts as in I:

$$\mathbf{A} = \mathbf{A}' + \mathbf{A}'' \quad (13)$$

where the elements of $\mathbf{A}''$ are

$$a''_{j,j} = 1 + \phi, j = 2, 3, \dots \quad (14a)$$

$$a''_{j,j+1} = a''_{j+1,j} = -\phi^{\frac{1}{2}}, j = 2, 3, \dots \quad (14b)$$

$$a_{i,j} = 0, |i-j| \geq 2 \quad (14c)$$

$$a_{1,j} = a_{j,1} = 0, j = 1, 2, \dots \quad (14d)$$

and the matrix $\mathbf{A}'$ is given by

$$\begin{aligned} \mathbf{A}' = & c_1 \mathbf{e}_1 \mathbf{e}_1^T + c_2 (\mathbf{e}_1 \mathbf{y}^T + \mathbf{y} \mathbf{e}_1^T) + c_3 \mathbf{y} \mathbf{y}^T + \\ & \kappa_1 (\nu_0^2 x_n / x_b + 1) \mathbf{e}_1 \mathbf{e}_1^T - (\kappa_1 \phi)^{\frac{1}{2}} (\mathbf{e}_1 \mathbf{e}_2^T + \mathbf{e}_2 \mathbf{e}_1^T) \end{aligned} \quad (15)$$

In eqn. (15) we have introduced the following new symbols:

$$c_1 = \kappa_1 x_n (h_1^2 + n^2 / x_1 - (n + \nu_0 - 1)^2) \quad (16a)$$

$$c_2 = (\kappa_1 \phi)^{\frac{1}{2}} x_n (h h_1 + n / x_1 - (n + \nu_0 - 1)) \quad (16b)$$

$$c_3 = \phi x_n (h^2 + 1 / x_1 - 1) \quad (16c)$$

$$\mathbf{y}^T = \{0, 1, \phi^{\frac{1}{2}}, \phi, \phi^{3/2}, \dots\} \quad (17)$$

A SIMILARITY TRANSFORMATION

The method used in I consists of two steps. First the matrix $\mathbf{A}$ is transformed into tridiagonal form by Lanczos' tridiagonalization algorithm, and then the complex susceptibility $\kappa(\omega)$ is computed as function of the frequency ω by a continued fraction expansion from the tridiagonal form. Here we shall keep the principles of the second step unchanged, while we shall find it more profitable to use another point of view on the first step.

The first step in I can alternatively be considered as a transformation to a new basis set which has been obtained by applying a Schmidt orthogonalization to the sequence of vectors $\mathbf{y}_1, \mathbf{e}_1, \mathbf{e}_2, \dots$, where

$$\mathbf{y}_1^T = \{1, \phi^{\frac{1}{2}}, \phi, \dots\}$$

The fact that in the present case the first reaction is different from the following reactions suggests that one should apply the Schmidt orthogonalization to the sequence

$$\mathbf{b}'_1, \mathbf{e}_1, \mathbf{e}_2, \dots, \text{ with } \mathbf{b}'_1 = \alpha \mathbf{e}_1 + \mathbf{y} \quad (18)$$

The parameter, α , is determined by the requirement that the vector $\mathbf{b}'_1$ should be parallel to the vector $\mathbf{Gf}$ of eqn. (10) in I; this choice secures that we can still find $\kappa(\omega)$ by just computing the (1,1)-element of the inverse of the matrix $\mathbf{C} + i\omega \mathbf{I}$ where $\mathbf{C}$ is the matrix given by eqn. (25) below. The desired value of α is

$$\alpha = (f_1/f) (\kappa_1/\phi)^{\frac{1}{2}} \quad (19)$$

The Schmidt orthogonalization yields the following orthogonal vectors (besides $\mathbf{b}'_1$):

$$\mathbf{b}'_2 = \mathbf{e}_1 - \alpha(1 - \phi)\mathbf{y} \quad (20)$$

and for $j > 2$:

$$\mathbf{b}'_j = (1 - \phi) \sum_{k=2}^{j-2} \{\phi^{(k-2)/2} \mathbf{e}_k - \mathbf{y}\} + \phi^{(j-3)/2} \mathbf{e}_{j-1} \quad (21)$$

From this set we derive the orthonormal set, $\mathbf{b}_j (j=1, 2, \dots)$:

$$\mathbf{b}_j = \pi_j \mathbf{b}'_j \quad (22)$$

$$\pi_1 = \{(1 - \phi)/[1 + \alpha^2(1 - \phi)]\}^{1/2} \quad (23a)$$

$$\pi_2 = \{1 + \alpha^2(1 - \phi)\}^{-1/2} \quad (23b)$$

$$\pi_j = \phi^{-(j-2)/2}, j=3, 4, \dots \quad (23c)$$

Let $\mathbf{B}$ be the matrix whose columns are the vectors $\mathbf{b}_1, \mathbf{b}_2, \dots$; then $\mathbf{B}$ is unitary:

$$\mathbf{B}^T \mathbf{B} = \mathbf{I} \quad (24)$$

and we introduce the transformed matrix, $\mathbf{C}$, by

$$\mathbf{C} = \mathbf{B}^T \mathbf{A} \mathbf{B} \quad (25)$$

Since $\mathbf{A}$ is real and symmetric and $\mathbf{B}$ is real and unitary, then $\mathbf{C}$ is real and symmetric. The partition of $\mathbf{A}$ in $\mathbf{A}'$ and $\mathbf{A}''$ carries over to $\mathbf{C}$:

$$\mathbf{C} = \mathbf{C}^{(1)} + \mathbf{C}^{(2)} \quad (26)$$

$$\mathbf{C}^{(1)} = \mathbf{B}^T \mathbf{A}' \mathbf{B}, \quad \mathbf{C}^{(2)} = \mathbf{B}^T \mathbf{A}'' \mathbf{B} \quad (27)$$

By straight forward though tedious computations we find the following expressions for the elements of $\mathbf{C}^{(1)}$ and $\mathbf{C}^{(2)}$:

$$c_{11}^{(1)} = \pi_1^2 \alpha^2 c_1 + 2\pi_1^2 (1 - \phi)^{-1} \alpha c_2 + \pi_1^2 (1 - \phi)^{-2} c_3 + \kappa_1 \pi_1^2 \alpha^2 (v_0^2 x_n / x_b + 1) - 2(\kappa_1 \phi)^{1/2} \pi_1^2 \alpha \quad (28)$$

$$c_{12}^{(1)} = (1 - \phi)^{1/2} \pi_2^2 \alpha c_1 + \{(1 - \phi)^{-1/2} - \alpha^2 (1 - \phi)^{1/2}\} \pi_2^2 c_2 - \alpha (1 - \phi)^{-1/2} \pi_2^2 c_3 + (1 - \phi)^{1/2} \pi_2^2 \alpha \kappa_1 (v_0^2 x_n / x_b + 1) - \{(1 - \phi)^{1/2} - \alpha^2 (1 - \phi)^{3/2}\} \pi_2^2 (\kappa_1 \phi)^{1/2} \quad (29)$$

$$c_{13}^{(1)} = -\phi \alpha \kappa_1^{1/2} \pi_1 \quad (30)$$

$$c_{22}^{(1)} = \pi_2^2 c_1 - 2\pi_2^2 \alpha c_2 + \pi_2^2 \alpha^2 c_3 + \pi_2^2 \kappa_1 (v_0^2 x_n / x_b + 1) + 2\pi_2^2 (\kappa_1 \phi)^{1/2} \alpha (1 - \phi) \quad (31)$$

$$c_{23}^{(1)} = -\pi_2 \kappa_1^{1/2} \phi \quad (32)$$

$$c_{ij}^{(1)} = 0 \text{ if } i > 3 \text{ or } j > 3 \text{ or } i = j = 3 \quad (33)$$

$$c_{11}^{(2)} = \pi_1^2 \quad (34)$$

$$c_{12}^{(2)} = -(1 - \phi)^{3/2} \pi_2^2 \quad (35)$$

$$c_{13}^{(2)} = \pi_1 \phi^{1/2} \quad (36)$$

$$c_{22}^{(2)} = \alpha^2 (1 - \phi)^2 \pi_2^2 \quad (37)$$

$$c_{23}^{(2)} = -\alpha (1 - \phi) \phi^{1/2} \pi_2 \quad (38)$$

$$c_{jj}^{(2)} = 1 + \phi, j \geq 3 \quad (39)$$

$$c_{j,j+1}^{(2)} = -\phi^{1/2}, j \geq 3 \quad (40)$$

$$c_{1,j}^{(2)} = 0, j \geq 4 \quad (41a)$$

$$c_{i,j+1}^{(2)} = 0, j \geq 2, i \geq 2 \quad (41b)$$

The elements of $\mathbf{C}$ are then given by

$$c_{i,j} = c_{i,j}^{(1)} + c_{i,j}^{(2)} \quad (42)$$

Note that $\mathbf{C}$ is tridiagonal except for the fact that $c_{13} = c_{31}$ is different from zero:

$$c_{13} = \pi_1 \phi^{1/2} (1 - \kappa_1 f_1 / f) \quad (43)$$

A CONTINUED FRACTION EXPANSION

As in I the complex susceptibility, $\kappa(\omega)$ is, given by

$$\kappa(\omega) = (f^2 x_n \phi \pi_1^{-2}) \eta(\omega) \quad (44)$$

where $\eta(\omega)$ is the (1,1)-element of $(\mathbf{C} + i\omega \mathbf{I})^{-1}$. If $\mathbf{C}_j$ is the $j \times j$ matrix consisting of the first j columns and rows of $\mathbf{C}$ and $\mathbf{I}_j$ is the $j \times j$ unit matrix, then we can define $\eta_j(\omega)$ as the (1,1)-element of $(\mathbf{C}_j + i\omega \mathbf{I}_j)^{-1}$ and obtain $\eta(\omega)$ as the limit for $j \rightarrow \infty$ of $\eta_j(\omega)$. By the standard rule for calculating the inverse matrix $\eta_j(\omega)$ is given as the ratio between two determinants

$$\eta_j(\omega) = P_j(\omega) / Q_j(\omega) \quad (45)$$

$$P_j(\omega) = \text{Det}(\mathbf{C}'_{j-1} + i\omega \mathbf{I}_{j-1}) \quad (46)$$

$$Q_j(\omega) = \text{Det}(\mathbf{C}_j + i\omega \mathbf{I}_j) \quad (47)$$

where $\mathbf{C}'_{j-1}$ is obtained from $\mathbf{C}_j$ by deleting the first row and column.

From the almost tridiagonal form of $\mathbf{C}$ follows that for $j \geq 4$ both P_j and Q_j fulfil the recurrence relation

$$R_j(\omega) = (1 + \phi + i\omega) R_{j-1}(\omega) - \phi R_{j-2}(\omega) \quad (48)$$

If we introduce

$$x = \frac{1}{2}(1 + \phi + i\omega) / \sqrt{\phi} \quad (49)$$

then we can determine coefficients a_1, a_2, a_3 and a_4 such that for all $j \geq 2$

$$P_j(\omega) = \phi^{(j-2)/2} (a_1 U_j(x) + a_2 T_j(x)) \quad (50)$$

$$Q_j(\omega) = \phi^{(j-2)/2} (a_3 U_j(x) + a_4 T_j(x)) \quad (51)$$

Fig. 1. The imaginary part of $\kappa(\omega)$ as a function of $\log_{10}(\omega)$ for the parameters specified in eqn. (61) and $\kappa_1=1$, $f_1/f=1$. The four curves correspond in increasing order to $\gamma=0.002$, 0.005, 0.02 and 0.1.

Fig. 2. The imaginary part of $\kappa(\omega)$ as a function of $\log_{10}(\omega)$ for the parameters specified in eqn. (61) and $\kappa_1=0.1$, $f_1/f=1$. The four curves correspond in increasing order to $\gamma=0.002$, 0.005, 0.02 and 0.1.

Fig. 3. The imaginary part of $\kappa(\omega)$ as a function of $\log_{10}(\omega)$ for the parameters specified in eqn. (61) and $\kappa_1=0.01$, $f_1/f=1$. The five curves correspond to $\gamma=0.001$, 0.002, 0.005, 0.02 and 0.1. They can be identified by the fact that the right peak increases monotonously with γ . The curve for $\gamma=0.005$ only has one peak.

Fig. 4. The imaginary part of $\kappa(\omega)$ as a function of $\log_{10}(\omega)$ for the parameters specified in eqn. (61) and $\kappa_1=0.001$, $f_1/f=1$. The five curves correspond to $\gamma=0.001$, 0.002, 0.005, 0.02 and 0.1. The right peak increases monotonously with γ ; the left peak also appears to increase with γ , except for $\gamma=0.005$ where it does not exist.

where U_j and T_j are the Tschbyscheff polynomials

$$T_j(x) = \cos(jv) \quad (52)$$

$$U_j(x) = \sin[(j+1)v]/\sin v \quad (53)$$

$$\cos v = x \quad (54)$$

In fact, we have

$$a_1 = \phi^{-1}P_3(\omega)/x - P_2(\omega) \quad (55)$$

$$a_2 = 2P_2(\omega) - \phi^{-1}P_3(\omega)/x \quad (56)$$

$$a_3 = \phi^{-1}Q_3(\omega)/x - Q_2(\omega) \quad (57)$$

$$a_4 = 2Q_2(\omega) - \phi^{-1}Q_3(\omega)/x \quad (58)$$

Eqn. (54) can be solved for e^{iv}

$$e^{iv} = x + \sqrt{x^2 - 1} \quad (59)$$

If the sign of square root is defined by the convention that the real part of the square root should have the same sign as the real part of x , then e^{iv} is an analytic function of x outside a cut in the complex x -plane from -1 to 1 along the real axis and e^{iv} is numerically larger than one in this region. It is then a trivial matter to take the limit $j \rightarrow \infty$ and obtain

$$\eta(\omega) = \{(a_1 + \frac{1}{2}a_2)e^{iv} - \frac{1}{2}a_2e^{-iv}\} / \{(a_3 + \frac{1}{2}a_4)e^{iv} - \frac{1}{2}a_4e^{-iv}\}$$

$$\eta(\omega) = \{P_3(\omega) - \phi^{\frac{1}{2}}P_2(\omega)(x - \sqrt{x^2 - 1})\} / \{Q_3(\omega) - \phi^{\frac{1}{2}}Q_2(\omega)(x - \sqrt{x^2 - 1})\} \quad (60)$$

DISCUSSION

The computation of the real and the imaginary part of $\kappa(\omega)$ from eqns. (44), (60), (46) and (47) together with the equations of the earlier sections is in principle straight forward on a high speed computer as long as the necessary care is exercised to ensure that the programming is free of errors.

Since there are many free parameters, then the number of principally different cases is presumably large and we shall not try to be exhaustive, but rather show a few examples which take their origin in an actual application of the present model in the interpretation of experiments. The case we shall use is the ultrasonic absorption by a solution of *N*-methyl acetamide in carbon tetrachloride for which Rassing⁵⁻⁶ found that the following choice of parameters would fit the experiments

$$n = 2, \nu_0 = 0, K_1 = 46, K = 460, h = h_1 = 2 \quad (61)$$

$$\kappa_1 = 1, f_1/f = 1 \quad (62)$$

(the values of k_- and f only influences the scaling so we keep them equal to one). The computations by Rassing⁵ were done by cutting the matrix **A** down to a finite size and apply a numerical diagonalization; when these computations were compared with results obtained by using the formulas of the present article no significant deviations were found.

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In the examples we are going to consider we keep the parameters given in eqn. (61) fixed while we vary the two parameters given in eqn. (62). In all the cases we give plots which show the imaginary part of $\kappa(\omega)$ as a function of $\log_{10}(\omega)$ for various values of the brutto mol fraction of monomers, y ; i.e. the mol fraction of monomers if one assumes complete dissociation:

$$y = \sum_{j=1}^{\infty} jx_j / (1 + \sum_{j=2}^{\infty} (j-1)x_j) \quad (63)$$

The figures 1–4 show the effect of lowering κ_1 from 1 to 0.001 while f_1/f is kept fixed at 1. At the two highest values of κ_1 one has the same picture as in I; i.e. a single peak which separates into two peaks as the mol fraction increases. The peak at the high frequencies corresponds to the isolated eigenvalue which was discussed in I, while the peak at the lower frequencies corresponds to the continuous part of the spectrum of **A**. When κ_1 gets sufficiently small, then the rate of the reaction

deviates sufficiently from the rate of the other reactions to make this reaction appear as an isolated peak at low mol fraction. This has the interesting effect of making the peak at low frequencies raise at low and high mol fractions while it disappears at intermediate mol fractions.

The figures 5–8 show the effect of changing f_1/f while κ_1 is kept constant at 0.001. At low values of f_1/f ($f_1/f = 0.5$, Fig. 5) and high values of f_1/f ($f_1/f = 4$, Fig. 8) both peaks increase monotonously with the mol fractions, and the peak at low frequencies eventually becomes dominant. At $f_1/f = 1$ (Fig. 4) and $f_1/f = 3$ (Fig. 7) we have the above-mentioned “up-down-up” behaviour for the peak at low frequencies and the peaks have equal height at the highest mol fraction. Finally, in Fig. 6 at $f_1/f = 2$ ($=n$) the left peak shows an “up-down” behaviour and disappears totally at the highest mol fraction; except for the lowest mol fraction, the right peak dominates.

The very drastic changes in the pictures when f_1/f is changed carry an important message to persons who want to compare the results of different experimental situations.

Fig. 5. The imaginary part of $\kappa(\omega)$ as a function of $\log_{10}(\omega)$ for the parameters specified in eqn. (61) and $\kappa_1=0.001$, $f_1/f=0.5$. The five curves correspond to $y=0.001$, 0.002, 0.005, 0.01 and 0.04. Both peaks increase with y .

Fig. 6. The imaginary part of $\kappa(\omega)$ as a function of $\log_{10}(\omega)$ for the parameters specified in eqn. (61) and $\kappa_1=0.001$, $f_1/f=2$. The five curves correspond to $y=0.001$, 0.002, 0.005, 0.02 and 0.1. The right peak increases with y . The three highest values of the left correspond in decreasing order to $y=0.002$, 0.001 and 0.005.

Fig. 7. The imaginary part of $\kappa(\omega)$ as a function of $\log_{10}(\omega)$ for the parameters specified in eqn. (61) and $\kappa_1=0.001$, $f_1/f=3$. The five curves correspond to $y=0.001$, 0.002, 0.005, 0.02 and 0.1. The right peak increases with y . For the left peak the curves are in order of increasing height: $y=0.001$, $y=0.005$, $y=0.002$ (left) and $y=0.02$ (right), $y=0.1$.

Fig. 8. The imaginary part of $\kappa(\omega)$ as a function of $\log_{10}(\omega)$ for the parameters specified in eqn. (61) and $\kappa_1=0.001$, $f_1/f=4$. The five curves correspond to $y=0.001$, 0.002, 0.005, 0.02, 0.1. Both peaks increase with y .

When the experimental set-up is changed this will only cause minor changes in the matrix **A** (stemming from the changes in the vector **h** which seems to be rather unimportant); therefore, the eigenvalues and eigenvectors can be considered as essentially the same for all experiments. But the vector **f** which may be said to represent the measurement can easily be imagined to change significantly. As can be seen from Figs. 5–8 this can cause the peaks of the relaxation spectrum to show very different behaviour; a fact which is often assumed to occur only as a result of experimental errors.

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