revista mexicana de física 27 no. 4 (1981) 487-499

DERIVATION OF THE KIRCHHOFF—LANGEVIN EQUATION FOR A FLUID WITH A CHEMICAL REACTION

S.M.T. de la Selva

L.S. García-Colín *

Universidad Autónoma Metropolitana. Iztapalapa

Departamento de Física

México 13, D.F.

(recibido febrero 2,1981; aceptado marzo 9,1981)

ABSTRACT

This paper contains the derivation of the attenuation function for a fluid in which a chemical reaction takes place. The main result involves the explicit account of heat transport processes besides the ordinary viscous ones. The connection with experiment is briefly indicated in the context of previous work.

RESUMEN

Este trabajo contiene una deducción de la función de atenuación para un fluido en el cual ocurre una reacción química. El resultado principal involucra tomar en cuenta, explícitamente procesos de conducción de calor así como los procesos viscosos usuales. La conexión con el experimento se menciona brevemente en relación con trabajos publicados anteriormente.

---

* Miembro del Colegio Nacional

The purpose of this paper is to calculate the amplitude attenuation of plane waves F, in an infinite fluid in which a chemical reaction takes place, taking into account heat transfer and viscous processes. Diffusion processes will not be considered. The amplitude attenuation F for relaxing fluids has been shown[1,2] to be a quantity of physical interest in the evaluation of the bulk viscosity and the relaxation time. In (1) and (2) F was derived for the particular case in which heat transfer could be ignored. The present derivation takes this effect into account. The resulting equation is referred to as the Kirchhoff-Langevin equation. Since the wave vector $\vec{K}$ associated with the propagation of a sound wave in a fluid is usually complex, one can express the quantity F in terms of the imaginary part of $\vec{K}$, the amplitude attenuation coefficient α[3]. It is easily seen that[2]

$$F \equiv \frac{2\,\alpha/k}{1 - \alpha^2/k^2} \quad , \tag{1}$$

where k is the real wave vector.

To find an expression for F in terms of thermodynamical properties of the fluid, we start with the set of hydrodynamic equations given by[4], the continuity equation,

$$\frac{d\rho}{dt} = - \rho \operatorname{div} \vec{u} \quad . \tag{2}$$

Here, $\frac{d}{dt}$ is the substantial derivative, ρ the density and $\vec{u}$ the velocity of the center of mass of the fluid particle. The momentum conservation equation

$$\rho \frac{d\vec{u}}{dt} = - \operatorname{div}(\underset{\sim}{T} + p\ \underset{\sim}{1\!\!1}) \ , \tag{3}$$

where we have omitted any external force and $(\underset{\sim}{T} + p\ \underset{\sim}{1\!\!1})$ stands for the pressure tensor assumed to be symmetric. The energy balance equation

$$\rho\ \frac{d\varepsilon}{dt} = - \ (\underset{\sim}{T} + p\ \underset{\sim}{1\!\!1}):\operatorname{grad} \vec{u} - \operatorname{div} \vec{J}_Q \ , \tag{4}$$

where ε is the specific internal energy of the fluid particle and $\vec{J}_Q$ is the heat flow vector. The Gibbs relation

$$T\,\frac{ds}{dt} = \frac{d\varepsilon}{dt} - p\,\rho_0^{-2}\,\frac{d\rho}{dt} + T\left(\frac{\partial s}{d\xi}\right)_{\varepsilon,\rho}\frac{d\xi}{dt} \quad , \tag{5}$$

where T is the temperature, ρ_0 the equilibrium density, ξ the degree of advancement of the reaction and the quantity $T\left(\frac{ds}{d\xi}\right)_{\varepsilon,\rho}$ is the de Donder chemical affinity. This set of equations is complemented with the phenomenological relations for the flows $\underset{\sim}{T}$, $\vec{J}_Q$, $\frac{d\xi}{dt}$ and the equations of state. Succesively, these equations are

$$\underset{\sim}{T} \equiv (\Pi\underset{\sim}{1} + \overset{0}{\Pi}{}^s) = -\zeta\,\mathrm{div}\,\vec{u}\,\underset{\sim}{1} - \frac{L_{vr}}{T}A\underset{\sim}{1} - 2\eta(\mathrm{grad}\,\vec{u})^s \ , \tag{6}$$

$$\vec{J}_Q = -\lambda\,\mathrm{grad}\,T \ , \tag{7}$$

$$\frac{d\xi}{dt} = -\frac{L_{rr}}{\rho}A - \frac{L_{rv}}{\rho}\,\mathrm{div}\,\vec{u} \tag{8}$$

and

$$\begin{aligned} p &= p\,(\rho,A,s) \ , \\ \xi &= \xi\,(\rho,A,s) \ , \\ T &= T\,(\rho,A,s) \ . \end{aligned} \tag{9}$$

Here η is the shear viscosity, ζ the bulk viscosity, λ the heat conductivity, L_{rr} and L_{rv} the Onsager coefficients for the chemical reaction and the coupling of viscous and reactive processes respectively. Clearly, the coefficient L_{rv} is such that $|L_{vr}| = -|L_{rv}|$ [(4)].

In the so called acoustical approximation, the variables in the above set of equations are replaced by their linear deviations from equilibrium only. Indeed, in terms of their instantaneous values Z(t) and their average values, one has that

$$Z(t) = Z_0 + \tilde{Z}(t) \tag{10}$$

and quantities of second order in the deviations are neglected. Z_0 represents the equilibrium value of Z(t).

Thus, the set of hydrodynamic equations is transformed into the following linearized one, namely,

$$\frac{\partial\tilde{\rho}}{\partial t} = -\rho_o \operatorname{div}\vec{u} \quad , \tag{11}$$

$$\rho_o \frac{\partial\vec{u}}{\partial t} = -\operatorname{grad}\tilde{p} + \eta\Delta\vec{u} + \left(\frac{1}{3}\eta + \zeta\right)\operatorname{grad}\operatorname{div}\tilde{\vec{u}} + L_{vr}\operatorname{grad}\tilde{A}\,, \tag{12}$$

$$\rho_o \frac{\partial\tilde{\varepsilon}}{\partial t} = \lambda\,\Delta\tilde{T} + p_o\rho_o^{-1}\frac{\partial\tilde{\rho}}{\partial t} \quad , \tag{13}$$

$$T_o \frac{\partial\tilde{s}}{\partial t} = \frac{\partial\tilde{\varepsilon}}{\partial t} - \frac{p_o}{\rho_o^2}\frac{\partial\tilde{\rho}}{\partial t} \quad , \tag{14}$$

$$\frac{\partial\xi}{\partial t} = -\frac{L_{rr}}{\rho_o}\tilde{A} - \frac{L_{rv}}{\rho_o}\operatorname{div}\tilde{\vec{u}}\,, \tag{15}$$

$$\tilde{p} = \left(\frac{\partial p}{\partial A}\right)_{s\rho} dA + \left(\frac{\partial p}{\partial \rho}\right)_{sA} d\rho + \left(\frac{\partial p}{\partial s}\right)_{\rho A} ds\,,$$

$$\tilde{\xi} = \left(\frac{\partial \xi}{\partial A}\right)_{s\rho} dA + \left(\frac{\partial p}{\partial \rho}\right)_{sA} d\rho + \left(\frac{\partial \xi}{\partial s}\right)_{\rho A} ds \tag{16}$$

and

$$\tilde{T} = \left(\frac{\partial T}{\partial A}\right)_{s\rho} dA + \left(\frac{\partial T}{\partial \rho}\right)_{sA} d\rho + \left(\frac{\partial T}{\partial s}\right)_{\rho A} ds \quad .$$

One now assumes plane wave oscillations for the variables, that is,

$$\tilde{Z} = \hat{Z}\, e^{\,i(\omega t - Kx)} \quad , \tag{17}$$

where the complex number K is defined as

$$K \equiv k + i\alpha\,. \tag{18}$$

If we now take the Laplace-Fourier transforms of the set of equations (11)-(16) and make use of Eq.(17), one finds that

$$\omega\hat{\rho} = \rho_o\vec{K}\cdot\hat{\vec{u}}\,, \tag{19}$$

$$i\omega\rho_o\hat{\vec{u}} = i\vec{K}\hat{p} + \eta\vec{K}\cdot\vec{K}\hat{\vec{u}} + \left(\frac{1}{3}\eta + \zeta\right)\vec{K}(\vec{K}\cdot\hat{\vec{u}}) - i\vec{K}L_{vr}\hat{A}, \tag{20}$$

$$i\omega\rho_o\hat{\varepsilon} = \lambda\vec{K}\cdot\vec{K}\hat{T} + p_o\rho_o^{-1}\, i\omega\hat{\rho} \quad , \tag{21}$$

$$T_o\hat{s} = \hat{\varepsilon} - p_o\rho_o^2\hat{\rho} \quad , \tag{22}$$

$$i\omega\hat{\xi} = L_{rr}\rho_o^{-1}\,\hat{A} + L_{rv}\rho_o^{-2}\,i\omega\hat{\rho} \ , \tag{23}$$

$$\hat{p} = \left(\frac{\partial p}{\partial A}\right)_{\rho s}\hat{A} + \left(\frac{\partial p}{\partial \rho}\right)_{sA}\hat{\rho} + \left(\frac{\partial p}{\partial s}\right)_{\rho A}\hat{s} \quad ,$$

$$\hat{\xi} = \left(\frac{\partial \xi}{\partial A}\right)_{\rho s}\hat{A} + \left(\frac{\partial \xi}{\partial \rho}\right)_{sA}\hat{\rho} + \left(\frac{\partial \xi}{\partial s}\right)_{\rho A}\hat{s} \tag{24}$$

and
$$\hat{T} = \left(\frac{\partial T}{\partial A}\right)_{\rho s}\hat{A} + \left(\frac{\partial T}{\partial \rho}\right)_{sA}\hat{\rho} + \left(\frac{\partial T}{\partial s}\right)_{\rho A}\hat{s} \quad .$$

Combining Eqs. (19) and (20) we obtain that

$$\hat{p} - L_{vr}\,\hat{A} - \left[\frac{\omega^2}{K^2} + \frac{i\omega}{\rho_o}\left(\frac{4}{3}\eta + \zeta\right)\right]\hat{\rho} = 0 \quad , \tag{25}$$

and combining Eqs. (21) and (23),

$$i\omega\rho_o T_o\hat{s} - \lambda\vec{K}\cdot\vec{K}\hat{T} = 0 \quad . \tag{26}$$

The condition for the set of algebraic equations (23)-(26) to have a non-trivial solution is that determinant of the coefficients vanishes. Thus,

$$\begin{vmatrix} 1 & -L_{vr} & 0 & 0 & 0 & -\left(\dfrac{\omega^2}{K^2} + i\omega B\right) \\ 0 & 0 & 0 & i\omega\rho_o T_o & -\lambda K^2 & 0 \\ 0 & -L_{rr}/\rho_o & i\omega & 0 & 0 & -L_{rv}\rho_o^{-2}i\omega \\ 1 & -\left(\dfrac{\partial p}{\partial A}\right)_{\rho s} & 0 & -\left(\dfrac{\partial p}{\partial s}\right)_{\rho A} & 0 & -\left(\dfrac{\partial p}{\partial \rho}\right)_{sA} \\ 0 & -\left(\dfrac{\partial \xi}{\partial A}\right)_{\rho s} & 1 & -\left(\dfrac{\partial \xi}{\partial s}\right)_{\rho A} & 0 & -\left(\dfrac{\partial \xi}{\partial \rho}\right)_{sA} \\ 0 & -\left(\dfrac{\partial T}{\partial A}\right)_{\rho s} & 0 & -\left(\dfrac{\partial T}{\partial s}\right)_{\rho A} & 1 & -\left(\dfrac{\partial T}{\partial \rho}\right)_{sA} \end{vmatrix} = 0 \quad ,$$

which after expansion it transforms into

$$-i\omega\rho_o T_o \left\{ \left(- \frac{\partial p}{\partial \rho}\frac{L_{rr}}{\rho_o} + \frac{\partial p}{\partial A}\frac{L_{rv} i\omega}{\rho_o^2}\right) - i\omega\left(\frac{\partial p}{\partial A}\frac{\partial \xi}{\partial \rho} - \frac{\partial \xi}{\partial A}\frac{\partial p}{\partial \rho}\right) \right.$$
$$\left. - \frac{L_{rv}L_{vr}}{\rho_o^2} i\omega - \frac{L_{rr}}{\rho_o}\left(\frac{\omega^2}{K^2} + i\omega B\right) + i\omega\left(L_{vr}\frac{\partial \xi}{\partial \rho} - \frac{\partial \xi}{\partial A}\left[\frac{\omega^2}{K^2} + i\omega B\right]\right)\right\}$$
$$+ \lambda K^2 \left\{ i\omega\frac{\partial p}{\partial A} \times \left(\frac{\partial \xi}{\partial s}\frac{\partial T}{\partial \rho} - \frac{\partial T}{\partial s}\frac{\partial \xi}{\partial \rho}\right) - i\omega\frac{\partial \xi}{\partial A}\left(\frac{\partial p}{\partial s}\frac{\partial T}{\partial \rho} - \frac{\partial T}{\partial s}\frac{\partial p}{\partial \rho}\right)\right.$$
$$+ i\omega\frac{\partial T}{\partial A}\left(\frac{\partial p}{\partial s}\frac{\partial \xi}{\partial \rho} - \frac{\partial \xi}{\partial s}\frac{\partial p}{\partial \rho}\right) - \frac{\partial T}{\partial s}\left(\frac{L_{rr}}{\rho_o}\frac{\partial p}{\partial \rho} - \frac{\partial p}{\partial A}\frac{L_{rv} i\omega}{\rho_o^2}\right) \tag{27}$$
$$+ \frac{\partial p}{\partial s}\left(\frac{\partial T}{\partial \rho}\frac{L_{rr}}{\rho_o} - \frac{\partial T}{\partial A}\frac{L_{rv} i\omega}{\rho_o^2}\right) + i\omega\frac{\partial T}{\partial s}\left(L_{vr}\frac{\partial \xi}{\partial \rho} - \frac{\partial \xi}{\partial A}\left[\frac{\omega^2}{K^2} + i\omega B\right]\right)$$
$$\left. - i\omega\frac{\partial \xi}{\partial s}\left(\frac{\partial T}{\partial \rho}L_{vr} - \frac{\partial T}{\partial A}\left[\frac{\omega^2}{K^2} + i\omega B\right]\right) - \frac{\partial T}{\partial s}\left(\frac{L_{vr}L_{rv}}{\rho_o^2} i\omega - \frac{L_{rr}}{\rho_o}\left[\frac{\omega^2}{K^2} + i\omega B\right]\right)\right\} = 0 \ .$$

Here, B stands for the quantity $\frac{1}{\rho_o}(4/3\ \eta + \zeta)$. Introducing the Maxwell's relations

$$\left(\frac{\partial \xi}{\partial \rho}\right)_{As} = -\frac{1}{\rho_o^2}\left(\frac{\partial p}{\partial A}\right)_{\rho s} \tag{28}$$

and

$$\frac{1}{\rho_o^2}\left(\frac{\partial p}{\partial s}\right)_{A\rho} = \left(\frac{\partial T}{\partial \rho}\right)_{As} \quad , \tag{29}$$

and the definitions

$$\mathcal{T} \equiv \frac{\rho_o}{L_{rr}}\left(\frac{\partial \xi}{\partial A}\right)_{\rho,s} \quad , \tag{30}$$

$$C_{oo}^2 \equiv C_o^2 + \frac{\left[L_{rv} + \left(\frac{\partial p}{\partial A}\right)_{\rho,s}\right]^2}{\rho_o^2\left(\frac{\partial \xi}{\partial A}\right)_{\rho,s}} \tag{31}$$

and

$$C_o^2 \equiv \left(\frac{\partial p}{\partial \rho}\right)_{A,s} \tag{32}$$

into Eq. (27) and rearranging it, we obtain the following expression for the dispersion relation of sound waves:

$$
\begin{aligned}
\lambda K^4 \Bigg\{ & \left(\frac{\partial p}{\partial s}\right)^2_{A\rho} \rho_o^{-2}\, \mathcal{T}^{-1} - \left(\frac{\partial T}{\partial s}\right)_{A\rho} C_o^2\, \mathcal{T}^{-1} + \omega^2 B \left(\frac{\partial T}{\partial s}\right)_{A\rho} - \omega^2 \left(\frac{\partial A}{\partial \xi}\right)_{\rho s} \left(\frac{\partial \xi}{\partial s}\right)_{\rho A} \left(\frac{\partial T}{\partial A}\right)_{\rho s} B \\
& + i\omega \Bigg[C_{oo}^2 \left(\frac{\partial T}{\partial s}\right)_{\rho A} + 2 \left(\frac{\partial p}{\partial \xi}\right)_{\rho s} \left(\frac{\partial \xi}{\partial s}\right)_{\rho A} \left(\frac{\partial T}{\partial \rho}\right)_{As} - \left(\frac{\partial p}{\partial s}\right)_{A\rho} \left(\frac{\partial T}{\partial \rho}\right)_{As} \\
& - C_o^2 \left(\frac{\partial A}{\partial \xi}\right)_{\rho s} \left(\frac{\partial T}{\partial s}\right)_{\rho s} \left(\frac{\partial \xi}{\partial A}\right)_{\rho A} - 2\, \frac{L_{rv}}{\rho_o^2} \left(\frac{\partial A}{\partial \xi}\right)_{\rho s} \left(\frac{\partial p}{\partial s}\right)_{\rho A} \left(\frac{\partial T}{\partial A}\right)_{\rho s} + B \left(\frac{\partial T}{\partial s}\right)_{\rho A} \mathcal{T}^{-1} \Bigg] \Bigg\} \\
& + K^2 \Bigg\{ \omega^2 \rho_o T_o (C_{00}^2 + B\mathcal{T}^{-1}) + \left(\frac{\partial T}{\partial s}\right)_{A\rho} \omega^2\, \mathcal{T}^{-1} + i\omega \Bigg[\rho_o T_o C_o^2 \mathcal{T}^{-1} \\
& - \omega^2 \rho_o T_o \mathcal{T}^{-1} + \lambda\omega^2 \left(\frac{\partial T}{\partial \xi}\right)_{\rho s} \left(\frac{\partial \xi}{\partial s}\right)_{\rho A} - \left(\frac{\partial T}{\partial s}\right)_{\rho A} \Bigg] \Bigg\} - \omega^4 \rho_o T_o - i\,\omega^3 \rho_o T_o \mathcal{T}^{-1} = 0\ .
\end{aligned}
\tag{33}
$$

This equation may be written in the form

$$
\lambda K^4 (A + i\omega\pi) + K^2 [(C_1 + \lambda C_2) + i\omega (D_1 + \lambda D_2)] - I = 0
$$

or (34)

$$
\lambda K^2 [\, K^2 (A + i\omega\pi) + C_2 + i\omega D_2] + K^2 (C_1 + i\omega D_1) - I = 0 \quad ,
$$

where the meaning of the symbols A, π, C_1, C_2, D_1, D_2 and I is immediate after comparison of the coefficients between the terms in K^4, K^2 and K^0 in expressions (33) and (34).

To order $\lambda = 0$, this equation reduces to

$$
K_o^2\ (C_1 + i\omega D_1) - I = 0
$$

or

$$
K_o^2 = \frac{I}{C_1 + i\omega D_1} \quad .
$$

We now substitute K^2 by K_o^2 in the λ-term above, thus obtaining

$$\frac{\lambda I}{C_1 + i\omega D_1}\left[\frac{I}{C_1 + i\omega D_1}(A + i\omega\pi) + C_2 + i\omega D_2\right] + K^2(C_1 + i\omega D_1) - I = 0 \; .$$

From here, we immediatly arrive at

$$K^2 = \frac{I}{C_1 + i\omega D_1} - \frac{\lambda I}{(C_1 + i\omega D_1)^2}\left\{\frac{I}{C_1 + i\omega D_1}(A + \qquad C_2 + i\omega D_2\right\} \; . \tag{35}$$

We now proceed to the construction of Eq. (1), taking into account definition (18). First we separate the real *Re* from the imaginary *Im* part, then we form the ratios *Im*/*Re* and $2\alpha/k \big/ 1-\alpha^2/k^2$, equate them and finally we arrange the expressions in powers of the frequency. The result is the following one, namely,

$$\frac{2\,\alpha/k}{1-\alpha^2/k^2} = \omega\frac{\alpha_o\omega^{10} + \beta_o\omega^8 + \gamma_o\omega^6 + \delta_o\omega^4 + \varepsilon_o\omega^2 + \theta_o}{\alpha_o'\omega^{10} + \beta_o'\omega^8 + \gamma_o'\omega^6 + \delta_o'\omega^4 + \varepsilon_o'\omega^2 + \theta_o'}$$

$$\frac{+\,\lambda\,[a\omega^{10} + b\omega^8 + c\omega^6 + d\omega^4 + e\omega^2 + f\,]}{+\,\lambda\,[a'\omega^{10}+b'\omega^8+c'\omega^6+d'\omega^4+e'\omega^2+f']} \; , \tag{36}$$

where the meaning of the letters α_o, α_o', β_o, β_o', γ_o, γ_o', δ_o, δ_o', ε_o, ε_o', θ_o, θ_o', a, a', b, b', c, c', d, d', e, e', f and f' is listed in the appendix.

We now call

$$\frac{2\alpha/k}{1-\alpha^2/k^2} \equiv \omega\,\frac{P_{10} + \lambda R_{10}}{Q_{10} + \lambda S_{10}} \; , \tag{37}$$

where the quatities P_{10}, R_{10}, Q_{10} and S_{10} are read directly from Eq.(36). Then, by synthetic division, it is verified that for $\lambda = 0$, the ratio $\omega\, P_{10}/Q_{10}$ reduces to

$$\omega\,\frac{P_{10}}{Q_{10}} = \omega\,\frac{B + T(C_{oo}^2 - C_o^2) + \omega^2 B\,T^2}{C_o^2 + C_{oo}^2 T^2\omega^2} \; , \tag{38}$$

which is none other than the expression for the attenuation function F_A

previously derived[2]. From Eq.(32) and Eq.(33) we obtain finally that

$$\frac{2\ \alpha/k}{1-\alpha^2/k^2} = \omega\, \frac{\dfrac{Q_{10}[B + T(C_{00}^2 - C_0^2) + \omega^2\ B\ T^2]}{C_0^2 + C_{00}^2\ T^2\omega^2} + \lambda R_{10}}{Q_{10} + \lambda S_{10}}$$

or that

$$\frac{2\ \alpha/k}{1-\alpha^2/k^2} = \left[\omega\, \frac{B + T(C_{00}^2 - C_0^2) + \omega^2 T^2 B}{C_0^2 + C_{00}^2 T^2\ \omega^2} + \omega\lambda R_{10} Q_{10}^{-1}\right]\left[1 + \lambda \frac{S_{10}}{Q_{10}}\right]^{-1}. \tag{39}$$

Equation (39) is the Kirchhoff-Langevin equation, i.e., the sought relationship between the attenuation coefficient and the wave vector k [see Eq.(1)] with the frequency and the thermodynamic properties of the reactive fluid. When $\lambda = 0$ it reduces to the expression already obtained in Ref.2, where a method was presented whereby one can determine the transport coefficients ξ, L_{rr} and L_{rv} from the experimental sound attenuation data. Once these transport coefficients are known one may use Eqs.(39) to estimate the importance of the terms R_{10}/Q_{10} and S_{10}/Q_{10} which, as coefficients of the thermal conductivity contribution, are directly related to the heat transfer process in the relaxation region. However, this is by no means a simple task. Examination of Eqs.(36) and the expressions given in the Appendix will immediately reveal their complexity. This feature has strongly hampered any realistic or practical estimations of the heat transfer contribution.

CONCLUDING REMARKS

As we have pointed out in earlier stages of our work[1,2,5], the contribution of the coupling between the bulk viscosity and the chemical transport in a chemically reactive fluid is not just of an academic interest. Previous approaches to the problem of chemical relaxation processes using sound dispersion and attenuation have either neglected this effect by assuming that the bulk viscosity of the fluid is zero or by introducing the concept of an "effective viscosity" to explain part of the sound attenuation which cannot be accounted by the standard processes namely, shear and heat flows. This last approach to the question has the enormous disadvantage that such an effective viscosity has no clear physical meaning[5].

Our procedure which is essentially based on linear non-equilibrium thermodynamics leads to important results which we think clarify considerably the physical interpretation of chemical relaxation process. These results, of which Eq. (39) is the most general one, are:

i) The bulk viscosity ζ is shown to have a status of its own as a true transport coefficient free from any specific interpretation.

ii) The viscoreactive coefficients L_{rr} and L_{rv} have a strong bearing in the formula given in Eq. (39) accounting for the attenuation of sound.

iii) As we have insistently pointed out in Refs. 1, 2 and 5, the method commonly employed by physical chemists to measure the time relaxation of a one step reaction, finds its place within the framework of irreversible thermodynamics.

APPENDIX

The meaning of the coefficients of the polynomial is ω given in Eq. (31) in the text, is the following:

$$\alpha_o = \rho_o T_o B^5 \quad ,$$

$$\beta_o = \rho_o T_o B^3 (2C_{\infty}^4 + 5BT^{-1}(C_{\infty}^2 - C_o^2) + 3B^2T^{-2}) \quad ,$$

$$\gamma_o = \rho_o T_o B(-6C_{\infty}^4 C_o^2 BT^{-1} - 16C_{\infty}^2 C_o^2 B^2 T^{-2} - 10C_o^2 B^3 T^{-3} + C_{\infty}^8 + 6C_{\infty}^6 BT^{-1}$$
$$+ 12C_{\infty}^4 B^2 T^{-2} + 10C_{\infty}^2 B^3 T^{-3} + 3B^4 T^{-4} + 10C_o^4 B^2 T^{-2}) \quad ,$$

$$\delta_o = \rho_o T_o T^{-1} [(C_{\infty}^2 + BT^{-1})^5 + 6C_{\infty}^4 C_o^4 BT^{-1} + 18C_{\infty}^2 C_o^4 B^2 T^{-2} + 12C_o^4 B^3 T^{-3}$$
$$- C_{\infty}^8 C_o^2 - 8C_{\infty}^6 C_o^2 BT^{-1} - 18C_{\infty}^4 C_o^2 B^2 T^{-2} - 16C_{\infty}^2 C_o^2 B^3 T^{-3} - 5C_o^2 B^4 T^{-4}] \quad ,$$

$$\varepsilon_o = \rho_o T_o T^{-3}(-2C_{\infty}^4 C_o^6 - 8C_{\infty}^2 C_o^6 BT^{-1} - 6C_o^6 B^2 T^{-2} + 5C_o^8 BT^{-1} + 2C_{\infty}^6 C_o^4$$
$$+ 6C_{\infty}^4 C_o^4 BT^{-1} + 6C_{\infty}^2 C_o^4 B^2 T^{-2} + 2C_o^4 B^3 T^{-3}) \quad ,$$

$$\theta_o = \rho_o T_o C_o^8 T^{-5}(C_{oo}^2 - C_o^2 + BT^{-1}) \quad ,$$

$$\alpha_o' = \rho_o T_o C_{oo}^2 B^4 \quad ,$$

$$\beta_o' = \rho_o T_o B^2(2C_{oo}^6 + 4C_{oo}^4 BT^{-1} + 2C_{oo}^2 B^2 T^{-2} - 4C_o^2 C_{oo}^2 BT^{-1} + C_o^2 B^2 T^{-2}) \quad ,$$

$$\gamma_o' = \rho_o T_o(-4C_o^4 B^3 T^{-3} + 6C_o^4 C_{oo}^2 B^2 T^{-2} - 6C_{oo}^4 C_o^2 B^2 T^{-2} - 4C_{oo}^6 C_o^2 BT^{-1} + 2C_o^2 B^4 T^{-4}$$
$$+ C_{oo}^{10} + 4C_{oo}^8 BT^{-1} + 6C_{oo}^6 B^2 T^{-2} + 4C_{oo}^4 B^3 T^{-3} + C_{oo}^2 B^4 T^{-4}) \; ,$$

$$\delta_o' = \rho_o T_o(-4C_o^6 C_{oo}^2 BT^{-3} + 6C_o^6 B^2 T^{-4} + 2C_{oo}^6 C_o^4 T^{-2} - 6C_o^4 C_{oo}^2 B^2 T^{-4} - 4C_o^4 B^3 T^{-5}$$
$$+ C_{oo}^8 C_o^2 T^{-2} + 4C_{oo}^6 C_o^2 BT^{-3} + 6C_{oo}^4 C_o^2 B^2 T^{-4} + 4C_{oo}^2 C_o^2 B^3 T^{-5} + C_o^2 B^4 T^{-6}) ,$$

$$\varepsilon_o' = \rho_o T_o C_o^6 T^{-4}[C_{oo}^2 C_o^2 - 4C_o^2 BT^{-1} + 2(C_{oo}^2 + BT^{-1})^2] \quad ,$$

$$\theta_o' = \rho_o T_o C_o^{10} T^{-6} \quad ,$$

$$a = 0 \quad ,$$

$$b = \left(\frac{\partial p}{\partial s}\right)_{\rho A}^2 \frac{B^3 T^{-1}}{\rho_o^2} - t_1 B^2(2C_o^2 BT^{-1} - 2BT^{-1} C_{oo}^2 - 3C_{oo}^4 + 3C_o^2 C_{oo}^2)$$
$$+ t_2 B^2(3C_{oo}^2 + BT^{-1}) \quad ,$$

$$c = \left(\frac{\partial p}{\partial s}\right)_{\rho A}^2 \rho_o^{-2} BT^{-1}(-3C_o^2 BT^{-1} - 3C_{oo}^4 + 2B^2 T^{-2}) + t_1(3C_o^4 B^2 T^{-2} + 3C_{oo}^4 B^2 T^{-2}$$
$$- 6C_{oo}^4 C_o^2 BT^{-1} + 2C_{oo}^2 B^3 T^{-3} - C_{oo}^8 + C_o^2 C_{oo}^6 + 6C_o^4 C_{oo}^2 BT^{-1} - 6C_{oo}^2 C_o^2 B^2 T^{-2}$$
$$- 2C_o^2 B^3 T^{-3}) + t_2(-C_{oo}^6 + 3C_{oo}^4 BT^{-1} - 6C_o^2 C_{oo}^2 BT^{-1}$$
$$+ 6C_{oo}^2 B^2 T^{-2} + 2B^3 T^{-3}) .$$

Here, $t_1 \equiv \left(\frac{\partial \xi}{\partial s}\right)_{A\rho}\left(\frac{\partial T}{\partial \xi}\right)_{\rho s}$ and

$$t_2 \equiv 2\left(\frac{\partial p}{\partial \xi}\right)_{\rho s}\left(\frac{\partial \xi}{\partial s}\right)_{A\rho}\left(\frac{\partial T}{\partial \rho}\right)_{As} - \left(\frac{\partial p}{\partial s}\right)_{\rho A}\left(\frac{\partial T}{\partial \rho}\right)_{As} - 2L_{vr}\rho_o^{-2}\left(\frac{\partial T}{\partial \xi}\right)_{\rho s}\left(\frac{\partial p}{\partial s}\right)_{\rho A} .$$

$$d = \left(\frac{\partial p}{\partial s}\right)_{\rho A} \rho_o^{-2}(3C_o^4T^{-1} + 3C_{oo}^4C_o^2 - 6C_{oo}^2C_o^2BT^{-1} - 6C_o^2B^2T^{-2} - 3C_{oo}^4BT^{-1}$$

$$+ B^3T^{-3} - 2C_{oo}^6)T^{-2} + t_1(-3C_{oo}^6 + 3C_o^2B^2T^{-2} - 6C_{oo}^4BT^{-1} - 3C_o^4C_{oo}^2$$

$$- 3C_{oo}^2B^2T^{-2} + 6C_{oo}^2C_o^2BT^{-1} + 6C_o^2C_{oo}^4)C_o^2T^{-2} + t_2(3C_o^4C_{oo}^2 - 3C_o^4BT^{-1}$$

$$+ C_{oo}^6 + 3C_{oo}^4BT^{-1} + 3C_{oo}^2B^2T^{-2} + B^3T^{-3} - 6C_{oo}^2C_o^2BT^{-1} - 6C_o^2C_{oo}^4)T^{-2},$$

$$e = \left(\frac{\partial p}{\partial s}\right)_{\rho A}^2 \rho_o^{-2}(-6C_{oo}^2C_o^2 - C_o^4 + 3C_o^2BT^{-1} - 3C_{oo}^4 - 6C_{oo}^2BT^{-1}$$

$$- 3B^2T^{-2})C_o^2T^{-4} + t_1(C_{oo}^2 - C_o^2)C_o^6T^{-4} + t_2(2C_o^2 - 3BT^{-1} - 3C_{oo}^2)C_o^4T^{-4},$$

$$f = \left(\frac{\partial p}{\partial s}\right)_{\rho A}^2 \frac{C_o^6T^{-6}}{\rho_o^2},$$

$$a' = B^3(-t_2 - t_1[C_{oo}^2 - C_o^2]),$$

$$b' = \left(\frac{\partial p}{\partial s}\right)_{\rho A}^2 \frac{B^2T^{-1}}{\rho_o^2} + t_1(3C_{oo}^6 + 3C_{oo}^4BT^{-1} - 3C_o^4BT^{-1} - 3C_{oo}^4C_o^2)B$$

$$+ t_2(-2B^2T^{-2} + 3C_{oo}^4 + 3C_o^2BT^{-1})B,$$

$$c' = \left(\frac{\partial p}{\partial s}\right)_{\rho A}^2 \rho_o^{-2}(3C_{oo}^4BT^{-1} + 6C_{oo}^2B^2T^{-2} + 2B^3T^{-3} - 6C_{oo}^2C_o^2BT^{-1} - C_{oo}^6)T^{-1}$$

$$+ t_1(-C_o^2B^3T^{-3} - 3C_o^4B^2T^{-2} - 3C_o^4C_{oo}^2BT^{-1} + 3C_{oo}^6BT^{-1} + 3C_o^6BT^{-1}$$

$$+ 3C_{oo}^4B^2T^{-2} + C_{oo}^2B^3T^{-3} - 4C_o^2C_{oo}^6 + C_{oo}^8 - 3C_{oo}^4C_o^2BT^{-1} + 3C_{oo}^4C_o^4)T^{-1}$$

$$+ t_2(6C_{oo}^2C_o^2BT^{-1} + 6C_o^2B^2T^{-2} + 2C_{oo}^6 + 3C_{oo}^4BT^{-1} - B^3T^{-3}$$

$$- 3C_{oo}^4C_o^2 - 3C_o^4BT^{-1})T^{-1},$$

$$d' = \left(\frac{\partial p}{\partial s}\right)_{\rho A}^2 \rho_o^{-2}T^{-3}(-6C_o^2C_{oo}^4 - 6C_o^2C_{oo}^2BT^{-1} - 6C_o^4BT^{-1} + 3C_{oo}^2C_o^4$$

$$+ 3C_o^4BT^{-1} + C_{oo}^6 + 3C_{oo}^4BT^{-1} + 3C_{oo}^2B^2T^{-2} + B^3T^{-3}) + t_2(-6C_{oo}^2C_o^2$$

...

$$- 6C_o^2BT^{-1} + C_o^4 + 3C_o^2BT^{-1} + 3C_{oo}^4 + 6C_{oo}^2BT^{-1} + 3B^2T^{-2})C_o^2T^{-3}$$

$$+ t_1(4C_{oo}^2C_o^2 + 3C_o^2BT^{-1} - C_o^4 - 3C_{oo}^4 - 3C_{oo}^2BT^{-1})C_o^4T^{-3} \quad ,$$

$$e' = \left(\frac{\partial p}{\partial s}\right)_{\rho A}^2 \rho_o^{-2}C_o^4T^{-5}(2C_o^2 - 3C_{oo}^2 - 3BT^{-1}) - t_2C_o^6T^{-5}$$

$$+ \left(\frac{\partial T}{\partial s}\right)_{\rho A}(-3C_{oo}^2C_o^6T^{-5} - 3C_o^6BT^{-6} + 2C_o^8T^{-5}).$$

REFERENCES

1. S.M.T. de la Selva, L.S. García-Colín and J. Meixner, Adv. in Molec. Relax. and Int. Proc. 11 (1/2) (1977) 73-85.
2. S.M.T. de la Selva and L.S. García Colín, J. Chem. Phys. 72 (1980) 277.
3. L.D. Landau and E.M. Lifshitz, Fluid Mechanics, (Addison Wesley. Reading, Mass., 1959).
4. S.R. de Groot and P. Mazur Non-Equilibrium Thermodynamics (North-Holland Publ. Co. Amsterdam, 1962).
5. S.M.T. de la Selva and L.S. García-Colín, KINAM, 3 (1981) (in press)