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Irreversible Circulation and Orbital Revolution

——*Hard Mode Instability in Far-from-Equilibrium Situation*——

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The need and the use of the concept of *cyclic balance* and *irreversible circulation* are demonstrated by a chemically reacting system with two independent degrees of freedom. Under the presence of auto-catalytic channel, the reaction network may lead to instabilities at a certain threshold for the controllable major reactant. Attention is concentrated on the hard mode instability in particular, which leads to an orbital revolution of the distribution function. By looking at the evolution of fluctuation as well as the drift, one finds that the irreversible circulation becomes singular at the marginal situation. The resulting limit cycle is just a macroscopic manifestation of the dynamically directed property which is latent in the fluctuation below threshold. The state beyond the threshold is analyzed with Prigogine-Lefever-Nicolis model. Emphasis is placed on the fact that temporal oscillation is a new type of order which appears only far from equilibrium.

§ 1. Introduction

In a previous paper[1] the concept of irreversible circulation of fluctuation was proposed for the description of the state of a system of thermodynamically coupled degrees of freedom in a far from equilibrium situation. It was emphasized then that this concept is actually needed when there appears an instability through this circulation, in the sense that the resulting ordered state is just a macroscopic manifestation of this circulation, i.e. a limit cycle. To elucidate the content of this proposal, a simplest significant example is treated in this paper.

Although there may be any number of degrees of freedom according to the nature of the problem, the essential feature of physics involved may be seen by a two-dimensional example, in so far as one is interested in the instabilities, i.e. the behaviour of the system in the neighbourhood of the transition. When a stable steady state becomes destabilized a small number of fluctuating modes are expected to slow down, thus eventually dominating the whole situation. Essentially there are only two typical cases, i.e. (1) soft mode instability, which is familiar in thermodynamic equilibrium, and (2) hard mode instability,[2] which is associated with periodic variation in time, and is met only in far from equilibrium situation, i.e., in dissipative systems. In terms of the eigenvalues of regression rate matrix, a soft mode instability is associated with single real eigenvalue, which becomes vanishing. The marginal situation is then expected to be characterized essentially by this one degree of freedom. On the other hand, a hard mode instability is associated with a couple of conjugate imaginary eigenvalues at the marginal situa-

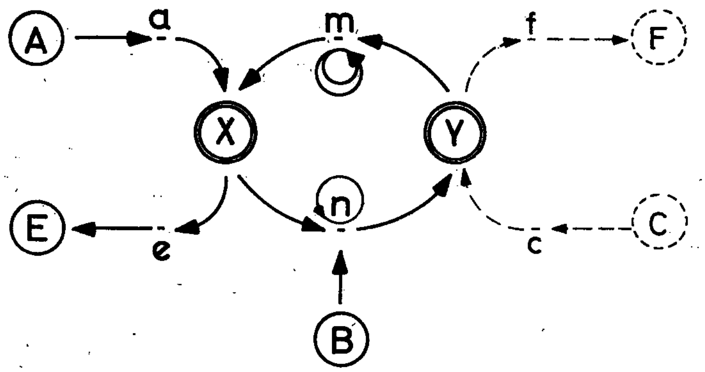

Fig. 1. Chemical reaction network with two independent reference reactants X and Y. Setting $k_c=k_f=0$, one finds a parallel model. A special case $m=2$ and $n=0$ corresponds to Prigogine-Lefever-Nicolis model.[3] Setting $k_c=k_e=k_m=0$ and adding an auto-catalysis m_a to channel a, one finds a series model. Special cases $m_a=n=1$, and $m_a=0$ and $n=2$ correspond to Lotka-Volterra model[5] and the simplified Higgins-Sel'kov model.[4]

tion. Accordingly a hard mode instability is characterized essentially by two degrees of freedom, between which things are to librate. In this sense a two-dimensional example is just enough to look into the marginal situation.

Introducing a concept of irreversible circulation α, a general treatment is given in § 2 of a system with two thermodynamically coupled degrees of freedom. It is then shown that the existence of autocatalysis, i.e. nonlinearity, plays a positive role in giving rise to a hard mode instability. The state beyond the threshold, i.e., the behaviour of ferro-cyclic phase is discussed in § 3, in which an order parameter is introduced, indicating the angular momentum of the orbital revolution.

As a concrete example which is not trivial, a chemical reaction network with two independent reference reactants, i.e. X and Y, is taken up, which is illustrated in Fig. 1. Here a dot i stands for a channel i with a forward rate coefficient k_i, and the encircled letters stand for the concentration of respective reactants. The backward reaction in each channel is neglected. This scheme includes Prigogine-Lefever-Nicolis model[3] (parallel type), simplified Higgins-Sel'kov model[4] (series type) and Lotka-Volterra model[5] as its special cases.

Explicit solutions of the nonlinear differential equations are obtained in § 4 specializing to the case of Prigogine-Lefever-Nicolis model.

Discussion is given in § 5, including that on the applicability of a uniform stochastic model adopted in this paper.

§ 2. General properties of a system with two degrees of freedom

——*Hard versus soft mode instability*——

Before going into a concrete example let us recapitulate the general theory and discuss the general properties of drift and variance expected in a system with two degrees of freedom.

As a method to treat these reactions a stochastic approach is adopted,[1] because one is interested in the nature of fluctuation as well as secular motion.

On the Markoffian assumption this reaction network is governed by a master equation

$$\frac{\partial}{\partial t}P(\boldsymbol{X},t)=\int\{W(\boldsymbol{X}-\Delta\boldsymbol{X},\Delta\boldsymbol{X})P(\boldsymbol{X}-\Delta\boldsymbol{X},t)-W(\boldsymbol{X},\Delta\boldsymbol{X})P(\boldsymbol{X},t)\}d\Delta\boldsymbol{X}.$$

The Kramers-Moyal expansion of this master equation acquires a realistic meaning, if one recognizes the local nature of transition, and introduces a scaling in terms of the system size parameter Ω. Namely by using

$$\left.\begin{array}{l}\boldsymbol{X}=\Omega\boldsymbol{x}=\varepsilon^{-1}\boldsymbol{x}\,, \quad (\varepsilon^{-1}\equiv\Omega),\\ \Omega^{d}P(\boldsymbol{X},t)=\psi(\boldsymbol{x},t) \ \text{ and } \ W(\boldsymbol{X},\Delta\boldsymbol{X})=\Omega w(\boldsymbol{x},\Delta\boldsymbol{X}),\end{array}\right\} \tag{1}$$

the Kramers-Moyal expansion of the above equation looks

$$\frac{\partial}{\partial t}\psi(\boldsymbol{x},t)=\sum_{n=1}^{\infty}\varepsilon^{n-1}\frac{1}{n!}\left(-\frac{\partial}{\partial\boldsymbol{x}}\right)^{n}\cdot c_n(\boldsymbol{x})\psi(\boldsymbol{x},t), \tag{2}$$

where

$$c_n(\boldsymbol{x})=\int d\Delta\boldsymbol{X}\,w(\boldsymbol{x},\Delta\boldsymbol{X})\,(\Delta\boldsymbol{X})^{n}. \tag{3}$$

Van Kampen[6] pointed out that the termination of (2) according to the apparent power of ε as it stands is not really consistent when the deviation from the most probable value stays microscopic. Introducing this idea by the transformation

$$\boldsymbol{x}=\boldsymbol{y}(t)+\varepsilon^{1/2}\boldsymbol{\xi} \ \text{ and } \ p(\boldsymbol{\xi},t)=\Omega^{1/2}\psi(\boldsymbol{y}(t)+\varepsilon^{1/2}\boldsymbol{\xi},t), \tag{4}$$

the final expansion according to the system size looks

$$\frac{\partial}{\partial t}p(\boldsymbol{\xi},t)-\Omega^{1/2}\dot{\boldsymbol{y}}(t)\cdot\frac{\partial p(\boldsymbol{\xi},t)}{\partial\boldsymbol{\xi}}$$
$$=\Omega\sum_{n=1}^{\infty}\varepsilon^{n/2}\frac{1}{n!}\left(-\frac{\partial}{\partial\boldsymbol{\xi}}\right)^{n}\cdot c_n(\boldsymbol{y}(t)+\varepsilon^{1/2}\boldsymbol{\xi})p(\boldsymbol{\xi},t). \tag{5}$$

One may choose the hitherto undetermined function $\boldsymbol{y}(t)$ in such a way that the lowest order term is cancelled, which leads to the equation

$$d\boldsymbol{y}/dt=c_1(\boldsymbol{y}(t)). \tag{6}$$

Retaining, then, the lowest order term in the remainder, one is left with a linear Fokker-Planck equation, i.e.

$$\frac{\partial}{\partial t}p(\boldsymbol{\xi},t)=-\frac{\partial}{\partial\boldsymbol{\xi}}\cdot\boldsymbol{G}(\boldsymbol{\xi},t), \tag{7}$$

where

$$G(\xi, t) = \mathsf{K}(y) \cdot \xi p(\xi, t) - (\mathsf{D}(y)/2) \cdot \frac{\partial}{\partial \xi} p(\xi, t)$$

is the probability flux, and

$$\mathsf{K}(y) = \{\partial c_1{}^i(y)/\partial y_j\} \text{ and } \mathsf{D}(y) = \{c_2{}^{ij}(y)\} \tag{8}$$

stand for the drift regression and diffusion in the probability distribution, respectively, and may depend on time through $y(t)$, which satisfies the kinetic equation (6).

From this master equation one may derive the evolution equations for a small deviation δy and the first and second moments,

$$\boldsymbol{\mu} \equiv \langle \xi \rangle \equiv \int d\xi p(\xi, t) \xi \quad \text{and} \quad \boldsymbol{\sigma} \equiv \langle \xi \xi \rangle \equiv \int d\xi p(\xi, t) \xi \xi ,$$

namely,

$$(d/dt)\delta y = \mathsf{K} \cdot \delta y , \tag{9}$$

$$(d/dt)\boldsymbol{\mu} = \mathsf{K} \cdot \boldsymbol{\mu} \tag{10a}$$

and

$$(d/dt)\boldsymbol{\sigma} = \mathsf{K}\boldsymbol{\sigma} + \widetilde{\mathsf{K}\boldsymbol{\sigma}} + \mathsf{D} , \tag{10b}$$

where tilde $\sim$ denotes the transposed matrix. Here (9) for δy describes the time course of small *non-stationary* deviation. One may argue that (10a) is redundant, because $\boldsymbol{\mu} = \langle \xi \rangle = 0$ in our approximation. Suppose, however, one observes a *sample* process of a spontaneous fluctuation from the most probable path $y(t)$. Then the time course of the average deviation $\langle \xi \rangle_c$ obeys (10a) with the use of a *conditional* probability distribution as $p(\xi, t)$.

In a stationary situation the fact that Eq. (9) coincides with Eq. (10a) provides a proof of the assumption made by Onsager.[7] The coincidence is by no means universal, and here it is the result of the system size expansion which assures the normal behaviour of the distribution function.

By the use of the shift $\boldsymbol{\mu}$ and variance $\boldsymbol{\sigma}$, the solution of the original Fokker-Planck equation may be written as

$$\left. \begin{aligned} & p(\xi, t) = [\det(\mathsf{g}(t)/2\pi)]^{1/2} \exp\{\phi(\xi, t)\}, \\ & \text{where} \\ & \phi(\xi, t) = -\tfrac{1}{2}(\xi - \boldsymbol{\mu}(t)) \cdot \mathsf{g}(t) \cdot (\xi - \boldsymbol{\mu}(t)) \\ & \text{and} \\ & \mathsf{g}(t)\boldsymbol{\sigma}(t) = 1 . \end{aligned} \right\} \tag{11}$$

In the present approximation one is to set $\boldsymbol{\mu} = 0$ hereafter.

2.1. *Drift evolution*

The secular drift $\boldsymbol{y}(t)$ obeys Eq. (6) and the steady state satisfies the condition $c_1(\boldsymbol{y}_s)=0$. The stability of the steady state may be discussed by looking at a small deviation $\delta\boldsymbol{y}$ from the steady state which obeys

$$(d/dt)\delta\boldsymbol{y}=\mathsf{K}_s\cdot\delta\boldsymbol{y}, \tag{12}$$

where

$$\mathsf{K}_s\equiv\mathsf{K}(\boldsymbol{y}_s)=\begin{pmatrix} K_{11}(\boldsymbol{y}_s) & K_{12}(\boldsymbol{y}_s) \\ K_{21}(\boldsymbol{y}_s) & K_{22}(\boldsymbol{y}_s) \end{pmatrix} \tag{13}$$

stands for the rate of drift regression. Setting

$$\delta\boldsymbol{y}(t)=e^{-\lambda t}\delta\boldsymbol{y}(0),$$

one finds a secular equation

$$\lambda^2+\Gamma\lambda+\Delta=0, \tag{14}$$

where

$$\Gamma\equiv K_{11}+K_{22}=\mathrm{Tr}\,\mathsf{K} \text{ and } \Delta\equiv K_{11}K_{22}-K_{12}K_{21}=\det\mathsf{K}. \tag{15}$$

Then λ is explicitly given by

$$\lambda_\pm=\{-\Gamma\pm\sqrt{\Gamma^2-4\Delta}\}/2, \tag{16}$$

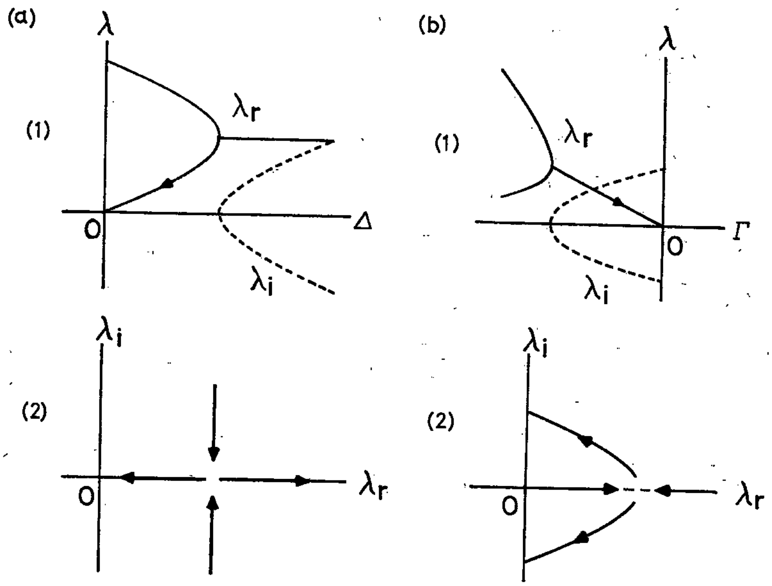

Fig. 2. Schematic representation of the eigenvalues as stability limit is approached: (a) Soft mode instability ($\Delta\to0$, for a given Γ), (b) hard mode instability ($\Gamma\to0$, for a given Δ). In Fig. (2) arrows indicate the motion of the eigenvalues in the complex λ-plane. ($\lambda=\lambda_r+i\lambda_i$)

from which one immediately recognizes that there are two different cases in which the real part of λ is to vanish.

i) $\varDelta\to 0(\varGamma<0)$

In this case λ has no imaginary part when $\varDelta$ becomes vanishing. This means that a single mode corresponding to λ_- becomes unstable, and this one mode dominates the behaviour of the whole system at marginal situation. This is the case of soft mode instability, which is popular in the analysis of phase transition in thermodynamic equilibrium. In fact this is the only type of instability which can be met in thermodynamic equilibrium, because the principle of microscopic reversibility applies to this case only.

In a far from equilibrium situation, however, a second type of instability may appear.

ii) $\varGamma\to 0(\varDelta>0)$

In this case a couple of modes, i.e. λ_+ and λ_-, become unstable at the same time and the two eigenvalues become purely imaginary and conjugate to each other. In other words the transition has essentially a two-dimensional character at the marginal situation. This new species may be called a "hard mode instability",[2] which is characteristic only to far from equilibrium situation. Appearance of this new type instability implies that the detailed balance does not hold in this case, and the overall balance should be called a *cyclic balance* instead. The eigenvalues $\lambda_\pm=\pm i\sqrt{\varDelta}$ stand for the frequency of an undamped drift rotation, of which the sense is determined by the sign of

$$\rho\equiv(\mathrm{rot}\,\delta\dot{y})_z=K_{21}-K_{12}\,. \tag{17}$$

2.2. *Evolution of variance*

The variance $\boldsymbol{\sigma}(t)$ around the secular drift is governed by (10b), and the steady state solution is given by

$$\boldsymbol{\sigma}_s=-\mathsf{K}^{-1}(\mathsf{D}+2\boldsymbol{\alpha})/2\,; \tag{18}$$

where

$$\boldsymbol{\alpha}\equiv(\widetilde{\mathsf{K}\boldsymbol{\sigma}}-\mathsf{K}\boldsymbol{\sigma})/2\equiv\alpha\begin{pmatrix}0 & 1\\ -1 & 0\end{pmatrix} \tag{19}$$

stands for the angular momentum

$$\alpha=\tfrac{1}{2}\langle[\boldsymbol{\xi}(0),\dot{\boldsymbol{\xi}}(0)]\rangle=\tfrac{1}{2}\langle\boldsymbol{\xi}(0)\times\dot{\boldsymbol{\xi}}(0)\rangle\,, \tag{20}$$

or the areal velocity of the irreversible circulation of fluctuation. In fact it can be shown that the angular momentum is conserved not only for the average over distribution but also along each stream line of the probability current. Alternatively $\boldsymbol{\alpha}$ is interpreted as the antisymmetric part of the Onsager kinetic coefficient L.

By requiring that $\boldsymbol{\sigma}$ is symmetric in (18), one may explicitly obtain $\boldsymbol{\alpha}$. In our particular case of two-dimension $\boldsymbol{\alpha}$ looks

$$\alpha=\{(K_{11}-K_{22})D_{12}+K_{12}D_{22}-K_{21}D_{11}\}/2\Gamma, \tag{21}$$

and in terms of α the variance σ_{ij} is expressed as

$$\left.\begin{aligned}\sigma_{11}&=\{K_{12}(D_{12}-2\alpha)-K_{22}D_{11}\}/2\Delta,\\ \sigma_{22}&=\{K_{21}(D_{12}+2\alpha)-K_{11}D_{22}\}/2\Delta,\\ \sigma_{12}&=\{K_{12}D_{22}-K_{22}(D_{12}+2\alpha)\}/2\Delta\\ &=\{K_{21}D_{11}-K_{11}(D_{12}-2\alpha)\}/2\Delta.\end{aligned}\right\} \tag{22}$$

Let us now focus our attention on the possible singularities appearing in the variance $\boldsymbol{\sigma}$. First of all every component of the variance involves the determinant $\Delta=K_{11}K_{22}-K_{12}K_{21}$ in the denominator. This means that $\Delta\to0$ corresponds to a diverging variance, which is an indication of instability. Clearly this corresponds to the soft mode instability as was defined in the previous section by drift evolution. In this case the time correlation function of the fluctuation is dominated by a single mode with purely real eigenvalue $\lambda_r\to0$, but the circulation $\boldsymbol{\alpha}$, although it is not vanishing by itself, is relatively unimportant, because of the essentially one-dimensional character of the system at marginal situation.

A second feature common to the components of variance is that they involve the irreversible circulation $\boldsymbol{\alpha}$. As is clear from the expression (21) for α, α will be divergent when $\Gamma=\mathrm{Tr}\,\mathsf{K}\to0$, which leads to a second instability of variance $\boldsymbol{\sigma}$. This corresponds clearly to the case of hard mode instability as defined in the previous section. From the point of view of the fluctuation this particular kind of instability is incurred through the pathological increase in the irreversible circulation, and a macroscopic circulation is expected to appear beyond the threshold. In this sense $\boldsymbol{\alpha}$ may in no way be neglected in the marginal situation, and the components of the variance are simply proportional to α in the marginal range of parameters, i.e.

$$\sigma_{11}\cong-K_{12}\alpha/\Delta,\ \sigma_{22}\cong K_{21}\alpha/\Delta \text{ and } \sigma_{12}\cong K_{11}\alpha/\Delta\cong-K_{22}\alpha/\Delta. \tag{23}$$

The trace of the variance is positive, therefore

$$\sigma_{11}+\sigma_{22}\cong\rho\alpha/\Delta>0. \tag{24}$$

This indicates that at marginal situation the sense of drift rotation ρ must coincides with that of irreversible circulation $\boldsymbol{\alpha}$, because Δ is expected to be positive definite. Furthermore, the average angular velocity of the *fluctuation*, defined by $\alpha/\sqrt{\det\boldsymbol{\sigma}}$, turns out to be identical with the *orbital* angular velocity $\sqrt{\Delta}$.

§ 3. States beyond the instability

In this section a qualitative discussion is given of the states beyond the instabilities, which were approached from the side of stable steady states in the previous section.

3.1. *States beyond the soft mode instability*

As only one degree of freedom dominates the behaviour of the system at marginal situation, the newly emerging state is expected to be a node which is asymptotically stable. The transition, therefore, corresponds to an exchange of stability[8] between the old and the new steady states, of which the latter is expected to be a static spatial pattern in wider sense. It will correspond to the eigenfunction belonging to the particular eigenvalue which characterizes the dominant asymptotic state. The new states may correspond either to a combination of species, or a spatially non-uniform pattern of concentration when the effect of spatial diffusion is included.

The discussion of stability of the new phase beyond the threshold from the point of view of the fluctuation is quite parallel to that of the phase below the threshold, and it is expected that the regression matrix to the spatial pattern will have a vanishing determinant as one approaches the transition from above.

3.2. *States beyond the hard mode instability*

This is essentially the case of two degrees of freedom at the marginal situation, which are characterized by a pair of conjugate eigenvalues of the regression matrix K. The state beyond the instability tends in most cases to a limit cycle $y(t)$ which obeys the equation

$$\frac{d}{dt}y(t)=c_1(y(t)) \quad \text{and} \quad y(t+T)=y(t). \tag{25}$$

As the right-hand side is generally non-linear in $y(t)$, the *orbital revolution* may be found only through numerical procedure.

Corresponding to the small scale circulation α of the distribution below the threshold, one may now introduce a measure for the macroscopic orbital revolution by

$$\mathsf{A}=\frac{1}{2}\overline{[y(t),\dot{y}(t)]}=\frac{1}{2}\overline{y(t)\times\dot{y}(t)}, \tag{26}$$

where

$$\bar{Q}\equiv\frac{1}{T}\int_0^T ds Q(s) \tag{27}$$

stands for the average over one cycle of revolution. The quantity A is the average angular momentum, or areal velocity of the orbital revolution.

As the instability is incurred through the probability circulation α, which becomes increasingly large when the transition is approached from below the threshold, the orbital revolution is naturally interpreted as a macroscopic manifestation of cyclic balance in the underlying mechanism, and as characteristic to far from equilibrium situation. In this sense the new phase may be called "ferro-cyclic" phase, which is characterized by an order parameter A, i.e. its angular momentum. The situation below threshold corresponds, then, to the "para-cyclic" phase, where the cyclic balance is latent.

One may still discuss the stability of the orbital motion by using the equation governing the small deviation, i.e.

$$(d/dt)\delta y = \mathsf{K}(y(t))\cdot\delta y, \tag{28}$$

where $y(t)$ is the solution of (25) which is periodic in time. In this case the overall stability is assured when

$$-\overline{\mathrm{Re}\,\lambda(t)} = \overline{\mathrm{Tr}\,\mathsf{K}(y(t))} = \overline{K_{11}} + \overline{K_{22}} \leq 0, \tag{29}$$

which is a condition due to Poincaré. The stability criterion for the steady state in the "para-cyclic" phase is a special case of this formula. Although

$$-\mathrm{Re}\,\lambda(y_s) = \mathrm{Tr}\,\mathsf{K}(y_s) > 0$$

in the ordered phase, it is expected that the above condition for the time averaged quantity is satisfied if the new phase is stable in wider sense.

The extension of the stochastic description to the case in which the coefficients in the linearized Fokker-Planck equation are time-dependent is just enough to discuss the situation in ferro-cyclic phase.

In treating the fluctuation under the presence of orbital revolution it is much simpler and more instructive to use a frame of reference which is moving with the orbital revolution itself. A natural choice of orthogonal frame is a set of the radial direction r and the tangential direction s as is shown in Fig. 3. The transformation matrix U from x-y frame*) to r-s frame is then given by

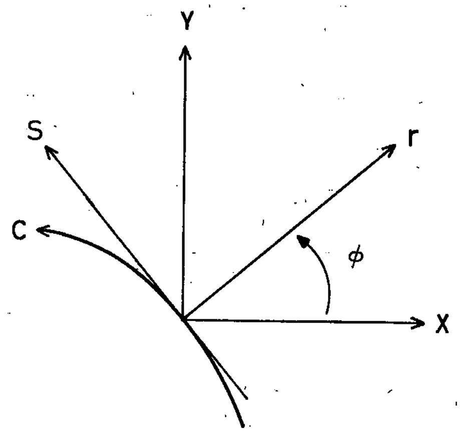

Fig. 3. Transformation from the static frame (x, y) to the moving frame (r, s). The s-axis is chosen as tangential to curve C, which is the most probable path determined by Eq. (25).

$$\mathsf{U}(t) = \begin{pmatrix} \cos\phi(t) & \sin\phi(t) \\ -\sin\phi(t) & \cos\phi(t) \end{pmatrix}, \tag{30}$$

and with this a vector $\boldsymbol{V}$ and a tensor T are transformed into $\boldsymbol{V}'$ and T' according to the following formulae, respectively:

$$\boldsymbol{V}' = \mathsf{U}(t)\cdot\boldsymbol{V} \text{ and } \mathsf{T}' = \mathsf{U}(t)\,\mathsf{T}\,\tilde{\mathsf{U}}(t), \tag{31}$$

where $\tilde{\mathsf{U}}$ is the transpose of U.

*) Here (x, y) are used instead of (x_1, x_2).

In order to separate the microscopic circulation from the macroscopic orbital revolution in pursuing temporal variation, the only point is that one has to take substantial time derivatives of relevant quantities, i.e.

$$\frac{d\boldsymbol{V}'}{dt}=\mathsf{U}\cdot\frac{d\boldsymbol{V}}{dt}+\frac{d\mathsf{U}}{dt}\cdot\boldsymbol{V}=\mathsf{U}\cdot\left(\frac{d\boldsymbol{V}}{dt}+\mathsf{R}\cdot\boldsymbol{V}\right) \tag{32}$$

and

$$\frac{d\mathsf{T}'}{dt}=\mathsf{U}\left(\frac{d\mathsf{T}}{dt}+\mathsf{RT}+\mathsf{T}\widetilde{\mathsf{R}}\right)\widetilde{\mathsf{U}}\,, \tag{33}$$

where

$$\mathsf{R}\equiv\frac{d\mathsf{U}}{dt}\widetilde{\mathsf{U}}=\frac{d\phi}{dt}\begin{pmatrix}0 & 1\\ -1 & 0\end{pmatrix} \tag{34}$$

stands for the rate of rotation of the frame itself.

Starting from (28) and (10b) one finds

$$\frac{d}{dt}\delta y'=(\mathsf{K}'+\mathsf{R})\cdot\delta y' \tag{35}$$

and

$$\frac{d}{dt}\sigma'=(\mathsf{K}'+\mathsf{R})\sigma'+\widetilde{(\mathsf{K}'+\mathsf{R})\sigma'}+\mathsf{D}', \tag{36}$$

where K' and D' are regression and diffusion matrices in the rotating frame, respectively.

By remembering that $\phi(t)$ is related to the velocity $\boldsymbol{v}(s)=c_1(y)$ of the orbital revolution through

$$\cos\phi(t)=v_y/v \text{ and } \sin\phi(t)=-v_x/v\,,$$

one finds

$$d\phi/dt=-K'_{rs}\,. \tag{37}$$

Based on this relation, the effective regression matrix $\mathsf{K}'+\mathsf{R}$ is now reduced, i.e.

$$\mathsf{K}'+\mathsf{R}=\begin{pmatrix}K'_{rr} & 0\\ K'_{sr}+K'_{rs} & K'_{ss}\end{pmatrix}, \tag{38}$$

which means that the regression in the transverse direction to the orbit is now separated. Suppose the limit cycle is stable, it follows naturally that K'_{rr} is negative definite, inspite of its temporal variation, and the periodicity assures $\overline{K'_{ss}}=0$, because $K'_{ss}=dv/ds$. Therefore the Poincaré condition for the overall stability of limit cycle is assured, i.e.

$$\overline{\mathrm{Tr}\,\mathsf{K}}=\overline{K'_{rr}+K'_{ss}}<0\,.$$

Using the relation (38) one may now write down evolution equations for the variance $\boldsymbol{\sigma}'(t)$ and the circulation $\boldsymbol{\alpha}'(t)$, i.e.

$$\frac{d}{dt}\sigma'_{rr}=2K'_{rr}\sigma'_{rr}+D'_{rr}, \tag{39a}$$

$$\frac{d}{dt}\sigma'_{rs}=(K'_{rr}+K'_{ss})\sigma'_{rs}+(K'_{sr}+K'_{rs})\sigma'_{rr}+D'_{rs}, \tag{39b}$$

$$\frac{d}{dt}\sigma'_{ss}=2K'_{ss}\sigma'_{ss}+2(K'_{rs}+K'_{sr})\sigma'_{rs}+D'_{ss} \tag{39c}$$

and

$$\begin{aligned}\boldsymbol{\alpha}'(t)&=[\widetilde{(\mathsf{K}'+\mathsf{R})\boldsymbol{\sigma}'}-(\mathsf{K}'+\mathsf{R})\boldsymbol{\sigma}']/2\\ &=\frac{1}{2}\left[(K'_{rs}+K'_{sr})\sigma'_{rr}+(K'_{ss}-K'_{rr})\sigma'_{rs}\right]\begin{pmatrix}0&1\\-1&0\end{pmatrix}.\end{aligned} \tag{40}$$

It is clear that σ'_{rr} may be treated as one separate dimension, which exhibits a normal behaviour. In other words the negative definite contribution of $2K'_{rr}\sigma'_{rr}$ and the positive definite contribution of D'_{rr} find a balance at finite σ'_{rr} in an asymptotic state. In fact one can prove that the periodic nature of K'_{rr} and D'_{rr} assures an asymptotic periodicity of σ'_{rr} in time. Given the solution σ'_{rr}, σ'_{rs} becomes also finite because the regression coefficient $\overline{K'_{rr}+K'_{ss}}$ is negative. If σ'_{rs} vanishes asymptotically, the variance becomes diagonal in the present moving frame.

As the circulation $\boldsymbol{\alpha}'(t)$ involves only σ'_{rr} and σ'_{rs}, it is expected that $\boldsymbol{\alpha}'(t)$ tends to a finite value, apart from a periodic time variation.

The behaviour of σ'_{ss} is clearly different. In this case, as K'_{ss} is purely periodic, i.e. $\overline{K'_{ss}}=0$, there is no negative definite contribution to $d\sigma'_{ss}/dt$, which means that σ'_{ss} increases, however slowly, because of the effect of D'_{ss}. As the rate is very small the periodic temporal variation of $y(t)$ may be observed over quite a number of cycles; however, the distribution is destined to diffuse along the orbit of limit cycle. Clearly this does not contradict to the stability of the limit cycle. In this sense the limit cycle may be described as quasi-stable, having asymptotic orbital stability and marginal phase instability. This increase of σ'_{ss} is essentially proportional to t, and is generally called "phase diffusion".*) When σ'_{ss} becomes macroscopic in size the original expansion (4)$\sim$(7) may no more be used; however, it may be shown that there will be no change of the distribution along the tangential direction in this limit if a new consistent expansion is introduced. (See Appendix)

*) In order to avoid confusion with spatial diffusion, we propose a new term "ensemble dephasing" for this phenomenon. (cf. § 5.)

§ 4. A concrete model (Prigogine-Lefever-Nicolis type)

One may start from the reaction network illustrated in Fig. 1, but discussion and calculations are restricted to the following specialized type:

$$\left.\begin{aligned} A &\xrightarrow{k_a} X\,, \\ X &\xrightarrow{k_e} E\,, \\ X+nY+B &\xrightarrow{k_n} (n+1)\,Y\,, \\ Y+mX &\xrightarrow{k_m} (m+1)\,X\,. \end{aligned}\right\} \tag{41}$$

Here m and n are also used as the multiplicities of auto-catalyses in reactions m and n, respectively.

The transition probability $w_i(x, y; \Delta X, \Delta Y)$ of channel i are given by

$$\left.\begin{aligned} &w_a(x, y; 1, 0) = k_a a\,, \\ &w_e(x, y; -1, 0) = k_e x\,, \\ &w_m(x, y; 1, -1) = k_m x^m y\,, \\ &w_n(x, y; -1, 1) = k_n bxy^n. \end{aligned}\right\} \tag{42}$$

Without loss of generality one may put all the rate constants equal to unity in order to simplify the calculation.

The secular motion is now governed by

$$\left.\begin{aligned} \frac{dx}{dt} &= x^m y - bxy^n + a - x\,, \\ \frac{dy}{dt} &= bxy^n - x^m y\,, \end{aligned}\right\} \tag{43}$$

from which the steady state is solved as

$$x_s = a \quad \text{and} \quad y_s = (a^{m-1}/b)^{1/(n-1)}. \tag{44}$$

Small deviation from the steady state satisfies the drift evolution equation (9), where regression matrix is given by

$$\mathsf{K} = \begin{pmatrix} (m-1)\,by_s{}^n - 1 & -(n-1)\,x_s{}^m \\ -(m-1)\,by_s{}^n & (n-1)\,x_s{}^m \end{pmatrix}. \tag{45}$$

The stability condition for the steady state (44) now looks

(i) $\Delta = (1-n)\,a^m > 0$

against the soft mode instability, and

(ii) $\Gamma = -\{1 + (1-n)\,a^m - (m-1)\,y_s a^{m-1}\} < 0$

against the hard mode instability.

In order to concentrate to the case in which there appears hard mode instability in particular let us set $n=0$. In order to find a hard mode instability it is needed according to (ii) that $m \geqq 2$. Let us specify $m=2$ and look into the concrete model after Prigogine, Lefever and Nicolis.[8]

The stable range corresponds to small values of b. On increasing b a marginal situation is attained for which

$$b=b_c \equiv a^2+1 . \tag{46}$$

For $b \geqq b_c$ the steady state is unstable against a hard mode instability, i.e. $\Gamma \geqq 0$.

In the para-cyclic phase, the critical slowing down of the drift regression is expressed by

$$\mathrm{Re}\,\lambda = -\Gamma = b_c - b ,$$

and the rate of drift rotation is given by

$$\mathrm{Im}\,\lambda \cong \sqrt{\Delta} = a .$$

The associated variance σ_{ij} and circulation α are given by

$$\left.\begin{aligned} \sigma_{xx} &= a(b_c+b)/(b_c-b), \\ \sigma_{yy} &= b(b_c+b)/(b_c-b)a, \\ \sigma_{xy} &= \sigma_{yx} = \alpha = -2ab/(b_c-b). \end{aligned}\right\} \tag{47}$$

When the variance σ is diagonalized, two eigenvalues are found to be

$$\begin{pmatrix} \sigma_M \\ \sigma_m \end{pmatrix} \cong \frac{2a^2+1 \pm \sqrt{4a^4+1}}{a} \left(\frac{b_c}{b_c-b} \right) \tag{48}$$

and

$$\alpha = -2ab/(b_c-b). \tag{49}$$

In Fig. 4 the inverses of variance and circulation are plotted as functions of the parameter b in the neighbourhood of transition.

It is clear that at the marginal situation the irreversible circulation $\boldsymbol{\alpha}$ is divergent as well as the variance $\boldsymbol{\sigma}$, and a macroscopic manifestation of this tendency is expected beyond the threshold.

This behaviour is parallel to that of the paramagnetic susceptibility χ as a function of temperature in the neighbourhood of Curie point, according to the molecular field theory.

4.1. *The ferro-cyclic phase*

The states beyond the threshold, i.e. the ferro-cyclic phase, may generally be accessed by numerical integration of the non-linear differential equations (43) with $m=2$ and $n=0$. The limit cycle solution has been found[8] as shown in Figs. 5 and 6(a).

The stability of the orbital revolution has been confirmed by the condition

$$\overline{\mathrm{Tr}\,\mathsf{K}(t)} = \overline{2x(t)y(t)} - (b+1+\overline{x(t)^2}) \leqq 0 , \tag{50}$$

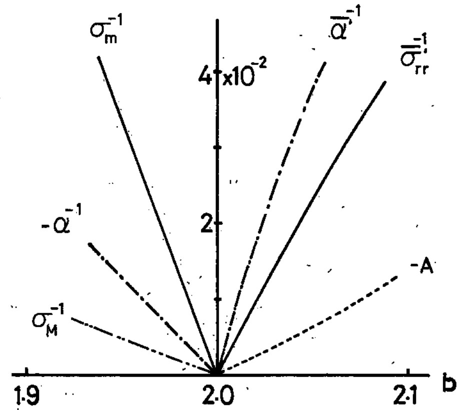

Fig. 4. Inverses of variance and circulation as functions of parameter b. ($a=1$) Below the threshold $b_c=2.0$, σ_M, σ_m and α are defined by (48) and (49). Above the threshold inverses of time average of σ'_{rr} and α' are plotted which are defined by (39a) and (40). The order parameter A is defined by (26), for which the scale is reduced to 1/5.

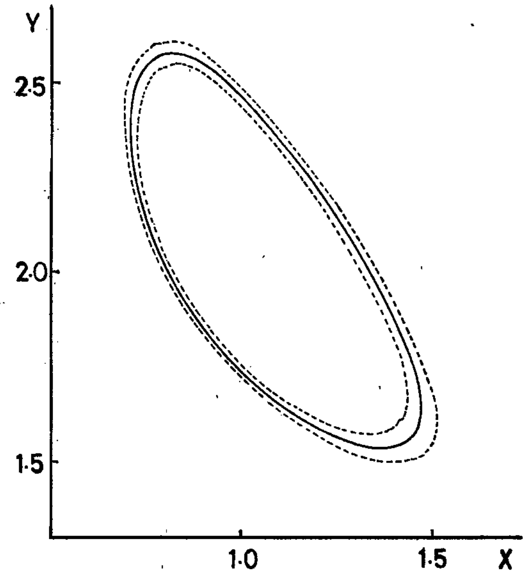

Fig. 5. Limit cycle and limit gully. The full line is the limit cycle. The dashed lines represent the relative magnitude of the transverse fluctuation, i.e., limit gully. (See the Appendix.) The parameters are chosen to be $a=1.0$ and $b=2.1$.

where the regression matrix $\mathsf{K}(t)$ is given by

$$\mathsf{K}(t)=\begin{pmatrix} 2x(t)y(t)-b-1 & x(t)^2 \\ b-2x(t)y(t) & -x(t)^2 \end{pmatrix}. \tag{51}$$

In Fig. 4 the order parameter $A(b)$ is shown as a function of the parameter $b \geqq b_c$. It can be shown that A is proportional to $b-b_c$ at least in the neighbourhood of the transition.

One now proceeds to the evaluation of fluctuation, which again is a function of time, due to the orbital revolution. The variance $\boldsymbol{\sigma}(t)$ is governed by Eq. (10), where $\mathsf{K}(t)$ is given by (51) and the phase diffusion matrix $\mathsf{D}(t)$ is given by

$$\mathsf{D}(t)=\begin{pmatrix} x(t)^2y(t)+a+x(t)+bx(t) & -x(t)^2y(t)-bx(t) \\ -x(t)^2y(t)-bx(t) & x(t)^2y(t)+bx(t) \end{pmatrix}. \tag{52}$$

After solving the variance $\boldsymbol{\sigma}(t)$ the circulation $\alpha(t)$ is expressed as

$$\alpha(t)=\{(b-2xy)\sigma_{xx}-x^2\sigma_{yy}-(2xy-b-1+x^2)\sigma_{xy}\}/2\,. \tag{53}$$

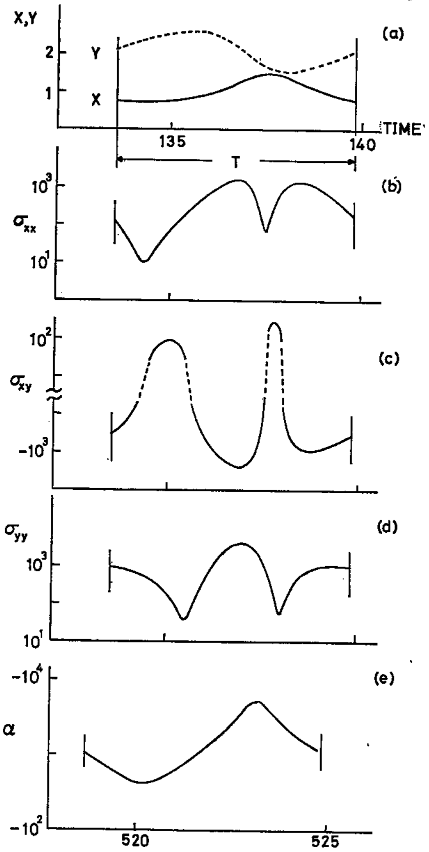

Fig. 6. Numerical results of most probable path (a), variances σ_{xx} (b), σ_{xy} (c), σ_{yy} (d) and circulation α (e) for one period of limit cycle, determined by Eqs. (25), (10) and (53), respectively. ($a=1.0$, $b=2.1$) All the quantities except for (a) are subject to a small but secular increase.

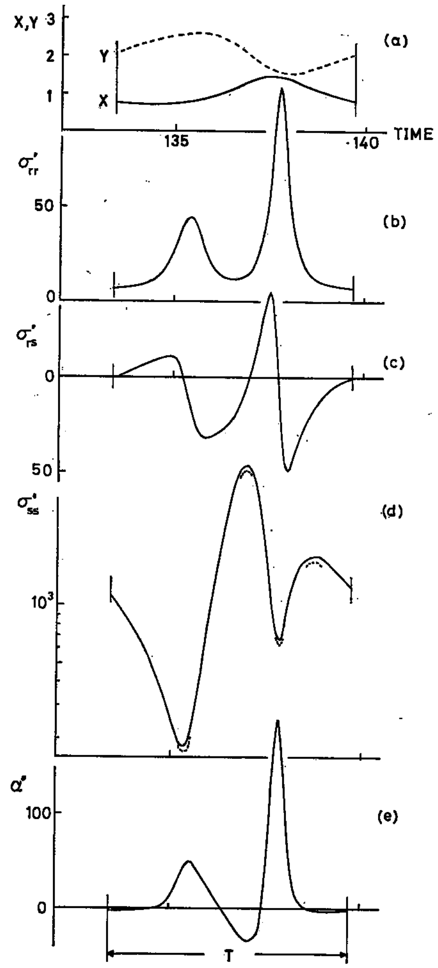

Fig. 7. Behaviour of the variances σ'_{rr} (b), σ'_{rs} (c), σ'_{ss} (d) and circulation α' (e) in the moving frame (r, s). $\sigma'(t)$ and $\alpha'(t)$ are calculated by using (39) and (40), respectively. ($a=1.0$, $b=2.1$) In Fig. (d) the dashed line represents σ'_{ss} two periods earlier. Other quantities are strictly periodic.

The results of numerical calculation are given in Fig. 6. As a result of the orbital revolution all the quantities of fluctuation appearing in Fig. 6 behaves roughly periodic. In closer examination, however, a small secular increase is noted in every element of variance and circulation. This is an indication of ensemble dephasing.

A more sensible frame of reference is the one that is rotating with the orbital revolution, as was described in § 3 and Fig. 3. The natural direction are then r and s, which are normal and tangential to the local orbit, respectively. Looked from this moving frame the asymptotic behaviour of the transverse variance σ'_{rr} is strictly periodic in time as shown in Fig. 7(b). It should also be noted that σ'_{rr} is positive definite. This is a result expected in the previous section. The same arguments apply to the cross variance $\sigma'_{rs}=\sigma'_{sr}$, and its asymptotic behaviour is also strictly periodic as shown in Fig. 7(c). The only difference is that σ'_{rs} may have either sign depending on the phase along the orbit.

As there exists no negative contribution to the time rate of the longitudinal variance σ'_{ss}, there results a secular increase in addition to a periodic variation. As was discussed in the previous section it is only for σ'_{ss} that there remains a secular increase in addition to a periodic variation as shown in Fig. 7(d).

It was found by diagonalizing the variance that the secular increase is confined to the greater eigenvalue $\sigma_M(t)$, and the smaller eigenvalue $\sigma_m(t)$ is practically periodic. It was verified that $\sigma'_{rr}(t)$ is always very close to $\sigma_m(t)$ and in fact coincides with it when σ'_{rs} becomes vanishing. This indicates clearly that the axes of the ellipse of variance are actually rotating, the longer axis trying to keep tangential to the orbit. This is only approximate, however, because σ'_{rs} exhibits non-zero values, though its time average is fairly small. It is also consonant that $\sigma'_{ss}(t)$ is found to be rather close to $\sigma_M(t)$ both in its magnitude and its change in time.

The real merit of the moving frame lies in the fact that it allows a definition of "residual circulation" $\alpha'(t)$, which is free from secular increase, as was discussed in the previous section. Actual results are shown in Fig. 7(e).

In order to discuss the ferro-cyclic phase, it is appropriate to define time averages of relevant quantities over one period of revolution. One may thus define $\overline{\sigma_{ij}}$ and $\overline{\alpha'}$ according to (27), and investigate their behaviour as functions of the controllable parameter b, as was done in the para-cyclic phase. Although they cannot be expressed in simple formulae definite results are obtained, which are shown in Fig. 4 as a ferro-cyclic counterpart of already mentioned para-cyclic quantities. Using a perturbation expansion in terms of $(b-b_c)/b_c$, one finds that

$$(\overline{\sigma_m})^{-1}\simeq(\overline{\sigma'_{rr}})^{-1}\simeq\frac{b-b_c}{b_c}, \tag{54}$$

in the post-critical neighbourhood of the transition. It is also found that

$$(\overline{\alpha'})^{-1}\simeq\frac{2}{2a^2-2a+1}\left(\frac{b-b_c}{b_c}\right), \tag{55}$$

which, when combined with the results for $A(b)\simeq-(2a^2/(a^2+2))(b-b_c)$, leads to a relation

$$\overline{\alpha'}\cdot A\simeq-\frac{(a^2+1)(2a^2-2a+1)}{a^2+2}=\text{const} \tag{56}$$

in the neighbourhood of the transition, which is alternatively written as

$$\overline{\langle \boldsymbol{\xi} \times \dot{\boldsymbol{\xi}} \rangle} \cdot \overline{[\boldsymbol{y}(t) \times \dot{\boldsymbol{y}}(t)]} = \text{const}\,. \tag{57}$$

This relation is very similar to the relation

$$\chi \cdot M_s^{2} = \text{const}\,,$$

or

$$\langle \Delta\boldsymbol{\mu} \cdot \Delta\boldsymbol{\mu} \rangle \langle \boldsymbol{M} \cdot \boldsymbol{M} \rangle = \text{const}\,,$$

which one finds for a ferromagnetic transition in the mean field approximation. The significance of the quantity $\boldsymbol{A}(b)$ as an order parameter for ferro-cyclic phase is quite clear from this parallelism.

§ 5. Discussion

In writing down the transition probability for a concrete model, gas kinetic cross section formulae were adopted in § 4. As there have been comments on this procedure in relation to the validity of local equilibrium, short discussion seems appropriate here. As was discussed by Kuramoto,[9] the essential point is the scale of measurement under consideration, hence an introduction of spatial inhomogeneity is needed. As will be shown elsewhere in detail the variance $\boldsymbol{\sigma}(q)$ associated with a wave number q is given by

$$\boldsymbol{\sigma}(q) = -\tfrac{1}{2}(\mathsf{K} - \boldsymbol{\Lambda} q^2)^{-1}(\mathsf{D} + 2\boldsymbol{\Lambda} q^2 \mathsf{y}_0 + \boldsymbol{\alpha}(q)),$$

where $\boldsymbol{\Lambda}$ is the spatial diffusion constant and y_0 is the steady state solution, both being diagonal matrices. $\boldsymbol{\alpha}(q)$ is the corresponding irreversible circulation.

Suppose a measurement with short enough wave length under a given diffusion $\boldsymbol{\Lambda}$ and a non-singular $\boldsymbol{\alpha}(q)$. Then one may attain a situation in which the effect of spatial diffusion dominates that of reaction. In this case one expects that $\boldsymbol{\sigma}(q) \simeq \mathsf{y}_0$, which is the normal Einstein relation assuring the stability and justifies the local equilibrium picture for short wave measurements. The gas kinetic cross section formula is only natural in this case provided the concentration is not too high.

Suppose now a measurement with long enough wave length. Then there may be cases in which the contribution of reaction dominates that of diffusion, i.e.

$$\boldsymbol{\sigma}(q) \simeq \boldsymbol{\sigma}(0) = -\tfrac{1}{2}\mathsf{K}^{-1}(\mathsf{D} + 2\boldsymbol{\alpha}),$$

which is just the result obtained by neglecting spatial diffusion and has nothing to do with the Einstein relation. It is not surprising, therefore, that in this particular limit one may find instability, side by side the stability of short wave.

As a result of the above consideration the use of gas kinetic cross section combined with a scheme without including spatial diffusion is justified, provided it may be interpreted as a long wave limit of a formulation for which the local equilibrium is assured, and the result is applied to modes having global scale only.

Irreversible circulation α may not be needed quantitatively when a relation

$$L_{ij}+L_{ji}\gg|L_{ij}-L_{ji}| \qquad (i\neq j)$$

exists among the components of Onsager coefficient. In the present notation this corresponds to a relation $\mathsf{D}\gg\alpha$, which is expected in two typical cases. When the relevant scale q^{-1} of measurement is small enough D involves a large term which is proportional to $\Delta q^2 \mathsf{y}_0$, as was shown earlier, thus dominating a finite α. It is only for a global scale measurement, therefore, that one may expect an appreciable contribution of the circulation α. Secondly, irrespective of the scale of measurement, circulation cannot appear in one dimension. In the case of soft mode instability essentially a single mode dominates the whole system at the marginal situation, thus the effect of the circulation α is expected to be small. In the case of hard mode instability, however, at least two degrees of freedom are degenerate, and the effect of the circulation α dominates the entire system at the marginal situation. In this paper stress has been placed on this last case, which does not seem to have been given due attention as it deserves.

Temporal oscillations are not rare in purely mechanical systems; however, the irreversible orbital revolution treated in this paper is an object of different nature. Let us dwell on the difference in what follows.

Technically, temporally periodic variations may be classified into two categories either mathematically or physically. With respect to the asymptotic scale of the oscillation, e.g., amplitude, they are classified mathematically into two categories, i.e., (A) a parametrized cycle family, or (B) a unique limit cycle. With respect to the physical origin or character of oscillation, e.g., frequency, they may be classified into two categories, i.e. (a) conservative oscillation, or (b) dissipative oscillation. Combining the two kinds of classifications one finds four different cases, i.e.

I. (A, a): Conservative cycle family,

II. (B, a): Conservative limit cycle,*)

III. (A, b): Dissipative cycle family,

IV. (B, b): Dissipative limit cycle.

It is clear that purely mechanical oscillation belongs to Case I; however, undamped mechanical oscillation of a closed system is always an idealization, and any real oscillating system is subject to dissipation, thus the oscillation is damped eventually, unless the system is driven from outside in a periodic way. The asymptotic state is a thermodynamic equilibrium, in which there remains no

*) The "frequency" is determined by conservative origin, but the asymptotic "amplitude" is determined by dissipation.

temporal change by definition.

The behaviour of a system having an influx of matter or energy from outside is quite different. The closest state to equilibrium one may find in this case is the steady state; however, it is only in the neighbourhood of equilibrium that this kind of state exhausts the possibility. For there may appear a *new* ordered phase which is associated with *undamped* temporal oscillation, as has been demonstrated earlier as a hard mode instability. All the remaining cases II, III and IV in the above classification belong to this category, and may be expected only at far from equilibrium situation. They are clearly different from purely mechanical oscillations in that they can only be induced in a dissipative system.

Ordinary lasing*) seems to belong to Case II, and also various kinds of driven clocks. The Lotka-Volterra model[5] for interacting populations seems to belong to Case III. The chemical oscillation treated in § 4 belongs to Case IV, and also the undamped spiking[10] in laser system.

As was shown in §§ 3 and 4, the limit cycle is associated in principle with the ensemble dephasing. However, it should be emphasized that it is experimentally possible to observe a *macroscopic sample* system which exhibits negligible dephasing. In the case of chemical reaction the synphasing agent may be either a natural diffusion against a volume reaction surrounding a local probe like microelectrode, or an artificial stirring of the whole system as is described by Zhabotinskii.[11] The spatially uniform oscillation may be detected in and only in this kind of macroscopic sample observation.

Although the appearance of a new type of order, i.e. limit cycle, was emphasized in this paper, actual situations require spatial order as well as temporal, as is clear from the experiments of Zhabotinskii et al.[11] Thorough discussion of the variety of induced orders in a non-uniform reacting system will be given in a forth-coming paper. Also a separate paper is in preparation to describe the Belousov-Zhabotinskii reaction.

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Appendix

Asymptotic state after ensemble dephasing

One may start from the system size expansion of the master equation (5) in (x_1, x_2) frame, and transform it into the curvilinear coordinate system (r, s).

*) As the oscillation behaves sinusoidal in the rotating wave approximation, one may alternatively visualize the lasing as a soft mode instability by a simple change of the frame of reference.

In the present case, however, fluctuations may be assumed microscopic only along transverse direction r, i.e.

$$r = r_0 + \varepsilon^{1/2}\rho\,, \tag{A1}$$

in which r_0 can be chosen as zero to specify the secular orbit. The differentiation is transformed into

$$\frac{\partial}{\partial x_i} = \varepsilon^{-1/2}\frac{\partial r}{\partial x_i}\frac{\partial}{\partial \rho} + \frac{\partial s}{\partial x_i}\frac{\partial}{\partial s}\,, \tag{A2}$$

in which it is clear that the term involving $\partial/\partial\rho$ is one order greater than the other terms.

Expanding with respect to ρ and retaining only terms of zeroth order in $\varepsilon^{1/2}$, one is left with

$$\frac{\partial}{\partial t}p(s,\rho;t) = -\frac{\partial}{\partial s}(v(s)p) - K(s)\frac{\partial}{\partial \rho}\rho p + \frac{1}{2}D(s)\frac{\partial^2}{\partial \rho^2}p\,, \tag{A3}$$

where

$$\left.\begin{aligned} &p(s,\rho;t) = \varepsilon^{-1/2}\psi(x_1(s,\varepsilon^{1/2}\rho), x_2(s,\varepsilon^{1/2}\rho);t), \\ &K(s) = K'_{rr}(s,0), \quad D(s) = D'_{rr}(s,0) \\ &v(s) = \{c_1^{x_1}(x_1,x_2)^2 + c_1^{x_2}(x_1,x_2)^2\}^{1/2}|_{r=0}\,. \end{aligned}\right\} \tag{A4}$$

and

One may easily separate r and s direction by putting

$$p(s,\rho;t) = n(s,t)f(\rho;s,t), \tag{A5}$$

where $f(\rho;s,t)$ is assumed as a normalized radial distribution. The resulting equations are

$$\frac{\partial}{\partial t}n(s,t) + \frac{\partial}{\partial s}(v(s)n(s,t)) = 0 \tag{A6}$$

and

$$\frac{\partial}{\partial t}f(\rho;s,t) + v(s)\frac{\partial f}{\partial s} = -K(s)\frac{\partial}{\partial \rho}\rho f + \frac{1}{2}D(s)\frac{\partial^2}{\partial \rho^2}f\,. \tag{A7}$$

Equation (A6) is clearly a continuity equation, therefore, the total probability is conserved along the orbit. By putting

$$f(\rho;s,t) = [2\pi\sigma(s,t)]^{-1/2}\exp[-\rho^2/2\sigma(s,t)], \tag{A8}$$

Eq. (A7) may be converted into an evolution equation for $\sigma(s,t)$;

$$\frac{\partial}{\partial t}\sigma(s,t) + v(s)\frac{\partial}{\partial s}\sigma(s,t) = 2K(s)\sigma(s,t) + D(s): \tag{A9}$$

and the true variance is given by

$$\langle\rho^2\rangle_{s,t}=n(s,t)\sigma(s,t). \tag{A10}$$

Let us introduce a new measure of distance along the orbit by

$$d\tau=ds/v(s), \tag{A11}$$

then Eqs. (A6) and (A9) become

$$\left(\frac{\partial}{\partial t}+\frac{\partial}{\partial\tau}\right)\hat{v}(\tau)\hat{n}(\tau,t)=0 \tag{A12}$$

and

$$\left(\frac{\partial}{\partial t}+\frac{\partial}{\partial\tau}\right)\hat{\sigma}(\tau,t)=2\hat{K}(\tau)\hat{\sigma}(\tau,t)+\hat{D}(\tau), \tag{A13}$$

where the sign $\wedge$ denotes

$$\hat{K}(\tau)\equiv K(s(\tau)) \text{ etc}.$$

In the moving frame, i.e. $\tau'=\tau-t$, these equations now look

$$\frac{\partial}{\partial t}\hat{v}(t+\tau')\hat{n}(t+\tau',t)=0 \tag{A12$'$}$$

and

$$\frac{\partial}{\partial t}\hat{\sigma}(t+\tau',t)=2\hat{K}(t+\tau')\hat{\sigma}(t+\tau',t)+\hat{D}(t+\tau'). \tag{A13$'$}$$

From Eq. (A12)$'$ one finds

$$\hat{v}(t+\tau')\hat{n}(t+\tau',t)=\hat{v}(\tau')\hat{n}(\tau',0),$$

or

$$\hat{v}(\tau)\hat{n}(\tau,t)=\hat{v}(\tau-t)\hat{n}(\tau-t,0). \tag{A14}$$

This indicates a macroscopic orbiting of an incompressible probability drop and the phase diffusion does not appear in this limit.

It can be shown that Eq. (A13)$'$ has a periodic asymptote with respect to t, because the initial memory is washed out by the regression coefficient $\hat{K}(\tau)<0$. This asymptote is just coincident with the stationary solution of (A13) under a periodic condition with respect to τ, i.e.

$$\frac{\partial}{\partial\tau}\hat{\sigma}(\tau)=2\hat{K}(\tau)\hat{\sigma}(\tau)+\hat{D}(\tau) \text{ and } \hat{\sigma}(\tau)=\hat{\sigma}(\tau+T), \tag{A15}$$

which might be called a *limit gully* and indicated by $\hat{\sigma}_g(\tau)$. Finally the asymptotic variance is given by (A10), i.e.

$$\langle\rho^2\rangle_{s,t}=n(s,t)\sigma_g(s).$$

It should be noted that even at the initial stage of phase diffusion, the variance along the radial direction is almost saturated in the limit gully, because the inhomogeneous linear equation (39a) for $\sigma'_{rr}(t)$ is essentially equivalent to Eq. (A15) or (A13)'.

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