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Some Remarks on the Theory of Fluctuations around Nonequilibrium States

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The recent comments by Y. Kuramoto [Prog. Theor. Phys. **49** (1973), 1782] on the theory of fluctuations in nonlinear chemical kinetics developed by Nicolis and Prigogine are discussed, and an answer to his objections is supplied. Some further results about the connection between the phase space description and the usual "birth and death" type description are presented. It is concluded that these two formalisms describe, respectively, the behavior of local fluctuations and of large scale, macroscopic fluctuations. An Einstein-like formula for the distribution of local fluctuations is recovered consistently.

§ 1. Introduction

In a recent series of papers, Prigogine and Nicolis[1),2)] have analysed the stochastic behavior of nonlinear chemical networks around steady states far from equilibrium. One of their main conclusions has been that the descriptions based on a birth and death type theory and on a more detailed phase space theory give rise generally to different results. The former predicts deviations of the probability distribution of fluctuations from the Poisson form. Moreover, in systems whose steady state lacks asymptotic stability the mean square deviation of fluctuations is shown to depend explicitly on time. In contrast the phase space description, supplemented with an initial *factorization* condition, predicts a universal behavior of *small*, local fluctuations given by a generalized Einstein formula. This result applies equally well to systems lacking asymptotic stability. Thus, according to the Prigogine-Nicolis analysis, the only way for such systems to evolve beyond the threshold for instability to a new regime is through a mechanism of large scale fluctuations, for which the birth and death description could again be applicable. So far these ideas have been illustrated on two models, a reaction involving a single intermediate and a bimolecular step and the autocatalytic set of reactions originally investigated by Volterra and Lotka.

At first sight it is indeed an unexpected result to find differences between the birth and death and the phase space formalisms. Therefore, we were not astonished when we became aware of a quite recent paper by Kuramoto,[3)] who criticized the Prigogine-Nicolis theory, and more specifically the factorization admitted by these authors to solve the phase space master equation. Using the same bimolecular model as in Refs. 1) and 2), he has derived equations for the first two moments of the probability distribution, which go beyond factorization.

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Assuming constant transition probabilities, he showed that the mean square deviation of the macroscopic variable (which in this model represents the number of particles of the chemical intermediate) is identical to the result of the birth and death analysis. Finally, Kuramoto expresses the opinion that a generalized Einstein formula for the probability of fluctuations cannot possibly explain the onset of chemical instabilities. The existence of the latter is well-established.[4]

The interesting comment of Kuramoto has motivated us to review here the whole subject and to include some recent results which were already announced in our previous papers.[1),2)] In § 2 we recall the main aspects of the phase space description of fluctuations. The structure of the phase space master equations is illustrated in § 3. The connection between the birth and death description and the phase space description of fluctuations is made explicit. It is shown that the phase space formalism enables one to treat correctly the behavior of *localized fluctuations*. Moreover, the comparative strengths of the elastic and reactive effects play a decisive role in the validity of these two formalisms. Section 4 is devoted to a qualitative analysis of the solutions of the phase space master equations. In the final section 5 some general comments are presented on the master equation description of fluctuations. The results derived in this paper provide an answer to the objections raised by Kuramoto, who apparently had not realized the fact that the Prigogine-Nicolis theory applies to the analysis of local fluctuations.

§ 2. The phase-space description of fluctuations

Consider an open nonlinear chemical reaction network and let $\{X\}$ denote the composition variables of the mixture. The macroscopic behavior of the system is described by the rate equations

$$\frac{dX}{dt} = V(X). \tag{2·1}$$

We assume that the mixture is dilute, and is maintained uniform. $V(X)$ denote the total change of X arising from chemical reactions containing the particular constituent under consideration. It is well known[4] that certain types of reactions described by (2·1), once driven far from equilibrium, exhibit unstable steady state solutions and evolve subsequently to a regime showing coherent behavior, e.g., in the form of temporal oscillations. In order to understand the *onset* of this coherent behavior it is necessary to analyze the behavior of fluctuations around the (unstable) nonequilibrium steady state.

What we want in fact is to analyze the behavior of such fluctuations in *macroscopic systems* involving a large number of degrees of freedom, N in a big volume, V such that $N \to \infty$, $V \to \infty$, $(N/V) =$ finite. The study of small systems is complicated by the fact that one needs corrections to the solutions of

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the master equations in powers of $1/V$.

We want moreover to restrict ourselves to *small* fluctuations, whose contribution to the second order excess entropy $(\delta^2 S)_0$ evaluated around the reference state is such that their probability remains appreciable. Suppose for a moment that, in spite of the fluctuations, the system remains homogeneous in space. By virtue of the central limit theorem, the probability distribution takes the form (assuming one remains below a critical point of instability):

$$P(\delta x) \propto \exp\left(-V\frac{\delta x^2}{2\sigma(\bar{x})}\right). \tag{2·2}$$

Here x is an *intensive* variable:

$$x=\frac{X}{V} \tag{2·3}$$

and the extensive variable X represents the number of particles of a reactant in the volume V. The variance $\sigma(\bar{x})$ depends on the average value, $\bar{x}$ of x, and is independent of the size of the system. Obviously, the only way for (2·2) to give rise to a nonvanishing probability is

$$\delta x \propto \frac{1}{V^{1/2}}. \tag{2·4}$$

Noting that V stands here for the size of the entire (macroscopic) system, we realize that a fluctuation obeying (2·4) is exceedingly small and cannot possibly influence the behavior of the system.

Consequently, a fluctuation

$$\delta x \propto a, \quad a=O(1) \tag{2·5}$$

occurring with a finite probability, where the factor a is now independent of the size of the entire system, will necessarily have to be *local*, i.e., to refer to a small part of the big system having a volume ΔV, such that $(\Delta V)^{-1/2}$ is of $O(1)$. But then, one should have to account for the coupling between this small subsystem and the remaining part of the big system, arising, e.g., from the exchange of matter across the V-ΔV interface. In different terms, because of the density fluctuations, the system will become locally inhomogeneous and the description based on (2·2) will break down.

Conversely, if one wants to maintain the picture of a homogeneous big system fluctuating appreciably in a coherent way, one will have to introduce large scale fluctuations of exceedingly small probability. In this respect we notice that in the work of Kuramoto, who adopts the picture of a homogeneous system, the very possibility of small fluctuations which precisely interest us here, is ruled out. A similar restriction to homogeneous systems is made automatically in the birth and death formalism.

It is remarkable that for linear systems or for systems near a (stable) equi-

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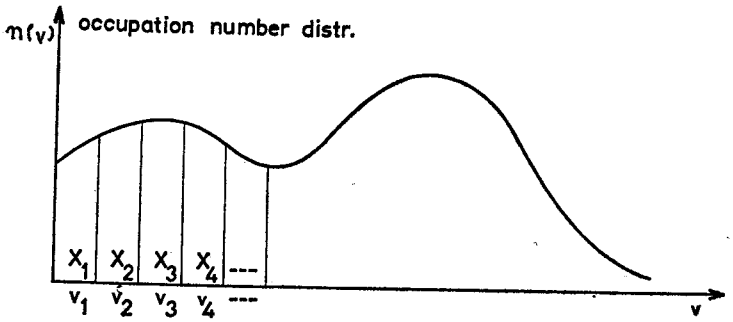

Fig. 1. Distribution of the occupation numbers as a function of velocity v in the general case of a variable *mean* velocity distribution.

librium state both ways to treat fluctuations are equivalent.[5] In different terms, there seems to be a "similitude" theorem applicable to these fluctuations, by virtue of which questions of size — and thus of homogeneity — do not matter. This property is a direct consequence of the absence of correlations between different reaction steps or between different degrees of freedom. These features are no longer found in nonlinear, nonequilibrium systems.

Having recognized the necessity of a local description of fluctuations far from equilibrium, we are led to adopt the phase space description where this local character is preserved. Let X_α be the number of particles of X in a phase-space volume Δr_α around the microscopic state α whose spectrum is taken discrete for simplicity (see Fig. 1). A random fluctuation of the macrovariable X will be expressed as

$$\delta X=\sum_\alpha \delta \dot{X}_\alpha \,. \tag{2·6}$$

The reference state $\overline{X}_\alpha$ will obey a kinetic equation of the Boltzmann type:

$$\frac{d\overline{X}_\alpha}{dt}=\sum_{\overline{r}} J_r(\overline{X}_\alpha, \overline{X}_\alpha')+\left(\frac{d\overline{X}_\alpha}{dt}\right)_{\mathrm{el}} . \tag{2·7}$$

Here, J_r describes the effect of reactive collisions. The elastic collision term $(d\overline{X}_\alpha/dt)_{\mathrm{el}}$ may be set approximately zero, if one deals with systems near a local equilibrium regime.

Assuming now that Eq. (2·7) defines a Markovian birth and death process in the *complete* phase space (including positions as well as internal states), one can derive a generalized master equation in this space in the form

$$\frac{dP(\{X_\alpha\},t)}{dt}=\sum_{\alpha\beta;\{X'\}} A_{\{X_\alpha\},\{X_\beta'\}} P(\{X_\beta'\},t). \tag{2·8}$$

In Refs. 1) and 2), this equation was solved in the limit of *small local fluctuations*. It was shown that the latter obey indeed a generalized Einstein distribution, with

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$$\overline{\delta X_\alpha \delta X_\beta'} = \delta^{K}_{\alpha\beta}\delta^{K}_{XX'}\overline{X}_\alpha . \tag{2·9}$$

The absence of correlations between degrees of freedom follows from the property (consistent with the limit of small local fluctuations) that the reduced probability functions $P_{1\cdots k}(X_{\alpha_1}, \cdots, X_{\alpha_k}, t)$ $(k<\infty)$ factorize over the various degrees of freedom. According to Eq. (2·6) then, the mean quadratic fluctuations of the macrovariable X also satisfy Einstein's relation *in this approximation*:

$$P(\delta X) \propto \exp[(\delta^2 S)_0/2k], \tag{2·10}$$

where k is Boltzmann's constant. For an ideal system this relation implies:

$$\overline{\delta X^2} = \overline{X} .$$

The implications of these conclusions in the problem of the onset of instabilities has been discussed in detail in Refs. 1) and 2). The crux of our argument has been the distinct behavior of local and of large scale fluctuations. It was argued that macroscopic instabilities (like chemical or fluid dynamical ones) cannot arise from a mechanism of local fluctuations, which will be damped by collisions. They require the nucleation (Ref. 2), p. 218) of large scale fluctuations which, once formed, behave in much the same way as in the birth and death description. In particular, in a state of marginal stability, these fluctuations will increase in time and drive the system to a new regime. As the probability of occurrence of such fluctuations is small in a system far from a region of phase transition, one should expect that the generalized Einstein relation will not be altered appreciably by these fluctuations.

§ 3. The connection between birth and death and phase space descriptions

In this section we illustrate some aspects of the phase space approach on an example considered in the previous papers by Prigogine and Nicolis:[1),2)]

$$A + M \overset{k_1}{\rightarrow} X + M ,$$

$$2X \overset{k_2}{\rightarrow} B + D . \tag{3·1}$$

A similar analysis has been carried out for the Volterra-Lotka model. The results are reproduced in the Appendix. The concentration of A, M, D, E are maintained constant. The macroscopic behavior of this system is summarized in Refs. 2) and 5). Suffice it to recall here that (3·1) admits a single asymptotically stable steady state corresponding to a (mean) number of particles of constituent X,

$$X_0 = \left(\frac{k_1 AM}{2k_2}\right)^{1/2} . \tag{3·2}$$

In order to discuss fluctuations around this state one must make an assumption about the type of stochastic process corresponding to (3·1). If the usual

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assumption of a birth and death process in the space of the number of particles of the *total* system is made, the following equation is derived for the corresponding probability distribution:[1),2)]

$$\frac{dP(X,t)}{dt}=k_1AM[P(X-1,t)-P(X,t)]$$

$$+k_2(X+1)(X+2)P(X+2,t)-k_2X(X-1)P(X,t). \qquad (3\cdot3)$$

In the limit of a "large system", $\bar{X}\to\infty$, this equation gives[1),2)]

$$\overline{\delta X^2}=\overline{(X-\bar{X})^2}\simeq\overline{(X-X_0)^2}=\frac{3}{4}X_0+O(1). \qquad (3\cdot4)$$

The factor 3/4 is specific to the model.

For the reason explained earlier this result appears to discard the local character of the fluctuations. In an effort to clarify further this point we consider, as in Refs. 1) and 2) and § 2, that reaction (3·1) involves a birth and death process in phase space. Setting X_α the number of particles in state α (see also Fig. 1), we want to derive an equation for the probability functions $P(\{X_\alpha\},t)$.

There are two basically different processes present. Firstly, there are elastic collisions, which do not change the total number of particles of constituent X but tend to redistribute the initial X_α's (see Fig. 1) according to the Maxwell-Boltzmann law (see Fig. 2). Secondly, there are reactive collisions, which change the number of particles of X present *and* modify the velocity distribution.

A central problem of chemical kinetics is therefore to account for the combined effects of these two processes. Several cases are conceivable, depending on the comparative strengths of the elastic and reactive effects. We can delineate three different limiting regions.

A. *Elastic effects are very weak.*

This corresponds to such problems as strongly exothermic reactions, or reactions in a rarified mixture. It may also describe adequately certain ecological situations involving competing populations where the ratio of predator versus prey is of the order of unity. The relevant equation is that of a stochastic process in phase and number space, but one where the velocity distribution is in no way centred on a Maxwell distribution. Essentially, each velocity region, and hence also the average populations in the various internal states evolve almost independently. For model (3·1) the equation describing this situation will be of the form

$$\frac{dP(\{X\},t)}{dt}=\sum_\alpha B_\alpha[P(X_\alpha-1,\{X'\},t)-P(X_\alpha,\{X'\},t)]$$

$$+\sum_{\alpha\beta}A_{\alpha\beta}[(X_\alpha+1)(X_\beta+1)P(X_\alpha+1,X_\beta+1,\{X'\},t)$$

$$-X_\alpha X_\beta P(X_\alpha,X_\beta,\{X'\},t)]. \qquad (3\cdot5)$$

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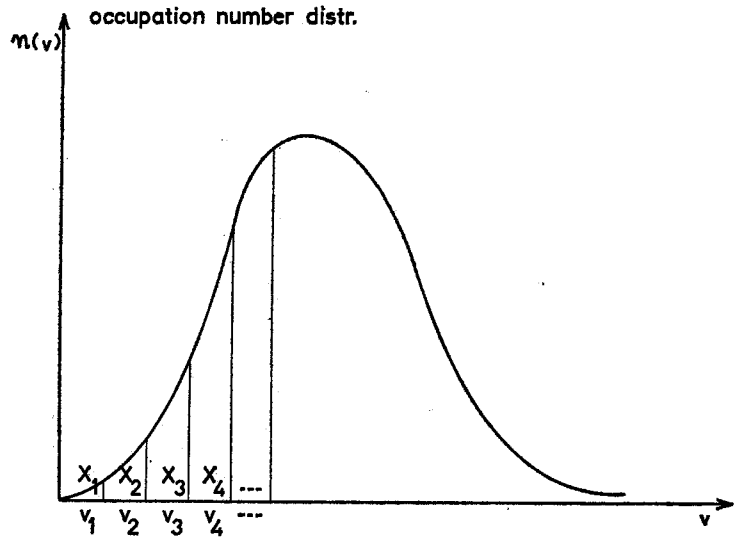

Fig. 2. Distribution of the occupation numbers as a function of velocity v when the velocity distribution is maintained in the Maxwellian form.

The notation is the same as in Refs. 1)~3). The coefficients B_α and $A_{\alpha\beta}$ are related to the transition probabilities B_{ijkl} and A_{ijkl} per unit time associated with the two steps in the reaction mechanism (3·1) as follows:

$$B_\alpha = \sum_{ijl} \bar{A}_i \bar{M}_j B_{ij\alpha l}\,,$$

$$A_{\alpha\beta} = \sum_{kl} A_{\alpha\beta kl}\,. \tag{3·6}$$

B. *Elastic effects are significant.*

In this case the stochastic process is centred around Maxwellian equilibrium. This leads to the equation

$$\begin{aligned}\frac{dP(\{X\},t)}{dt} &= \sum_\alpha B_\alpha'[P(X_\alpha-1,\{X'\},t)-P(X_\alpha,\{X'\},t)]\\ &+\sum_{\alpha\beta} A'_{\alpha\beta}[(X_\alpha+1)(X_\beta+1)P(X_\alpha+1,X_\beta+1,\{X'\},t)\\ &-X_\alpha X_\beta P(X_\alpha,X_\beta,\{X'\},t)]\\ &+\left(\frac{dP(\{X\},t)}{dt}\right)_{\mathrm{el}}.\end{aligned} \tag{3·7}$$

In principle one has to solve this equation by taking into account explicitly the effect of elastic collisions. A more straightforward and still fairly satisfactory procedure would be to say that elastic effects serve simply to establish *approximately* a Maxwell distribution, and that their explicit influence on the master equation can be neglected. This point of view has been adopted in the earlier

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publications by Prigogine and Nicolis.[1),2)] Equation (3·7) becomes

$$\frac{dP(\{X^e\},t)}{dt}=\sum_\alpha B_\alpha'[P(X_\alpha^e-1,\{X'^e\},t)-P(X_\alpha^e,\{X'^e\},t)]$$
$$+\sum_{\alpha\beta}A'_{\alpha\beta}[(X_\alpha^e+1)(X_\beta^e+1)P(X_\alpha^e+1,X_\beta^e+1,\{X'^e\},t)$$
$$-X_\alpha^eX_\beta^eP(X_\alpha^e,X_\beta^e,\{X'^e\},t)], \qquad (3\cdot8)$$

where the superscript "e" denotes that the various populations are centred around a Maxwellian (see Fig. 2). Notice that small fluctuations around the Maxwellian are allowed and are in fact essential to keep all the stochastic variables $\{X\}$ independent.

When Eq. (3·8) is solved with an additional initial factorization assumption, the Einstein formula (2·10) is recovered.[1),2)] It is to be noted that implicitly the factorization of the probability distribution assumes that the correlations between fluctuations of various degrees of freedom must be small. This in turn, can only be true for small, local fluctuations.

C. *Elastic Effects are dominant.*

In this limit thermal equilibrium is always, *rigorously* maintained, i.e., one neglects fluctuations of the velocity distribution. Thus, a chemical reaction can only provoke changes between equilibrium states with different total numbers of particles. As an example, the step of (3·1):

$$A+M\rightarrow X+M$$

produces one particle of X in some velocity state v_i, but the velocity distribution *immediately* relaxes from

$$\frac{Xv^2e^{-(\beta/2)v^2}}{Z_0}$$

to

$$\frac{(X+1)v^2e^{-(\beta/2)v^2}}{Z_0},$$

where Z_0 is a normalization constant. Thus, the whole process is *insensitive* to which velocity state *in fact* received the particle. As a result, the stochastic process in phase space degenerates to a process involving a single variable, the total number of particles of constituent X. The master equation becomes

$$\frac{dP(\{X\}^M,t)}{dt}=\sum_\alpha B_\alpha'[P(\{X+1\}^M,t)-P(\{X\}^M,t)]$$
$$+\sum_{\alpha\beta}A'_{\alpha\beta}[(X+1)^M(X+2)^MP(\{X+2\}^M,t)$$
$$-X^M(X-1)^MP(\{X\}^M,t)], \qquad (3\cdot9)$$

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where for example,

$$\{X+1\}^M=\{(X+1)v_1^2e^{-(\beta/2)v_1^2}dv_1,\ (X+1)v_2^2e^{-(\beta/2)v_2^2}dv_2,\ \cdots\}. \quad (3\cdot10)$$

We now define the quantities

$$k_1AM=\sum_\alpha B_\alpha',$$

$$k_2=\sum_{\alpha\beta}A'_{\alpha\beta}v_\alpha^2v_\beta^2\frac{e^{-(\beta/2)(v_\alpha^2+v_\beta^2)}}{Z_0^2}dv_\alpha dv_\beta. \quad (3\cdot11)$$

Then, Eq. (3·9) becomes *identical* to the birth and death master equation (3·3). This implies both the validity of the macroscopic result (3·2) and of the non-Poisson mean square deviation (3·4).*)

We see that the birth and death result is obtained by "freezing" the velocity distribution. We expect that this type of behavior will be representative of large scale fluctuations, which evolve in a time scale slow compared to the relaxation time of the velocity distributions. In contrast, local fluctuations of microscopic size, evolve too rapidly for this third type of behavior to be applicable. In a sense therefore, the usual birth and death description is *not* representative of the dynamics of a chemical system, but only of the evolution of the (infrequent) *large scale fluctuations.*

§ 4. The second moment approximation

We want now to solve Eq. (3·7) by extending our previous factorization assumption in taking correlations into account. To this end we consider the third moment of the probability distribution and assume the following decomposition:

$$\overline{X_1X_2X_3}=\overline{X}_1\overline{X}_2\overline{X}_3+\overline{X}_1M_{23}^X+\overline{X}_2M_{31}^X+\overline{X}_3M_{12}^X+M_{123}^X \quad (4\cdot1)$$

with

$$M_{123}^X\simeq0. \quad (4\cdot2)$$

Here the indices i refer to internal states and the M_{ij}^X, M_{ijk}^X are defined as

$$M_{ij}^X=\overline{(X_i-\overline{X}_i)\ (X_j-\overline{X}_j)},\ \text{etc.} \quad (4\cdot3)$$

It is expected that this decomposition will permit a first consistent treatment of *large scale* fluctuations, which were automatically discarded in the factorization assumption.

When the above relations are inserted into the moment equations of (3·7) a *closed* set of equations for $\overline{X}_\alpha, M_{\alpha\beta}^X$ is deduced. One finds

*) In actual fact Eqs. (3·10)~(3·11) are related to Kuramoto's example. As in his case, we also have here a set of "effective" transition probabilities per unit time, namely, k_1 and k_2 which are summed over, and thus become independent of the internal states.

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$$\frac{d\overline{X}_\alpha}{dt}=B_\alpha-2\sum_{j\neq\alpha}A_{\alpha j}\overline{X}_\alpha\overline{X}_j-2\sum_{j\neq\alpha}A_{\alpha j}M^{X}_{\alpha j}\,, \tag{4·4}$$

$$\frac{dM^{X}_{\alpha\alpha}}{dt}=B_\alpha+2\sum_{j\neq\alpha}A_{\alpha j}[-2\overline{X}_jM^{X}_{\alpha\alpha}-2\overline{X}_\alpha M^{X}_{\alpha j}+M^{X}_{\alpha j}+\overline{X}_\alpha\overline{X}_j]. \tag{4·5}$$

If, in addition, a steady state assumption is made for the first moments, Eq. (4·5) reads

$$\frac{dM^{X}_{\alpha\alpha}}{dt}=4\sum_{j\neq\alpha}A_{\alpha j}[-\overline{X}_jM^{X}_{\alpha\alpha}-\overline{X}_\alpha M^{X}_{\alpha j}+M^{X}_{\alpha j}+\overline{X}_\alpha\overline{X}_j]. \tag{4·6}$$

Finally

$$\begin{aligned}\frac{dM^{X}_{\alpha\beta}}{dt}=&-2M^{X}_{\alpha\beta}\sum_j(A_{\alpha j}+A_{\beta j})\overline{X}_j\\&-2\sum_{j\neq\alpha}A_{\beta j}M^{X}_{\alpha j}\overline{X}_\beta-2\sum_{j\neq\beta}A_{\alpha j}M^{X}_{\beta j}\overline{X}_\alpha\\&-2A_{\alpha\beta}[M^{X}_{\alpha\alpha}\overline{X}_\beta+M^{X}_{\beta\beta}\overline{X}_\alpha-\overline{X}_\alpha\overline{X}_\beta-M^{X}_{\alpha\beta}].\qquad(\alpha\neq\beta)\end{aligned} \tag{4·7}$$

By construction, all these relations are *local* through the indices α and β.

The crucial problem now is to estimate the order of magnitude of the corrections to the Einstein-like result brought by the second moment approximation. To this end we show that the moment equations (4·6) and (4·7) admit solutions of the form

$$\begin{aligned}&M^{X}_{\alpha\alpha}=\overline{X}_\alpha(1+O(\text{density})),\\&M^{X}_{\alpha j}=O(\text{density}).\end{aligned} \tag{4·8}$$

We first write the (local) equation (4·7) at the steady state in the form

$$\sum_{kl}\Lambda_{\alpha\beta,kl}M^{X}_{kl}=-A_{\alpha\beta}[M^{X}_{\alpha\alpha}\overline{X}_\beta+M^{X}_{\beta\beta}\overline{X}_\alpha-\overline{X}_\alpha\overline{X}_\beta], \tag{4·9}$$

where we set

$$\begin{aligned}\Lambda_{\alpha\beta,kl}=&(-A_{\alpha\beta}+\sum_j(A_{\alpha j}+A_{\beta j})\overline{X}_j)\delta^{Kr}_{k\alpha}\delta^{Kr}_{l\beta}\\&+\sum_{j\neq\alpha}A_{\beta j}\overline{X}_\beta\delta^{Kr}_{k\alpha}\delta^{Kr}_{lj}\\&+\sum_{j\neq\beta}A_{\alpha j}\overline{X}_\alpha\delta^{Kr}_{k\beta}\delta^{Kr}_{lj}\,.\end{aligned} \tag{4·10}$$

Note that in the limit of continuous spectrum Λ becomes a differential-integral operator over momenta *and* positions.

We see that the autocorrelations $M^{X}_{\alpha\alpha}$ contribute to the inhomogeneous terms of the equation (4·9) for M^{X}_{kl}. On the other hand, from Eq. (4·6) it is obvious that the deviation of $M^{X}_{\alpha\alpha}$ from the Einstein result: $M^{X}_{\alpha\alpha}=\overline{X}_\alpha$ can only be due to corrections arising from the cross correlations $M^{X}_{\alpha j}$. Assuming that the latter are smaller than $O(X_\alpha)$ we can substitute to first approximation in Eq. (4·9)

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the value of $M^X_{\alpha\alpha}$ given by Einstein's formula:

$$\underset{(4\cdot9)}{\text{r.h.s. of } (4\cdot9)} \simeq -A_{\alpha\beta}\overline{X}_\alpha\overline{X}_\beta\,. \tag{4·11}$$

The mean occupation numbers $\overline{X}_\alpha$ can be estimated as follows:[6]

$$\overline{X}_\alpha \simeq \frac{N}{V}\, x_\alpha \Delta \boldsymbol{r}_\alpha\,, \tag{4·12}$$

where V is the total volume of the system, N is the mean number of particles therein and the reduced variable x_α is a chemical composition variable (like molar fraction) multiplied by a distribution function of momenta and internal energies. Both N and V are macroscopic. Their ratio $n=(N/V)\ll 1$, as long as the system is not too dense.

Finally, it should be recalled that a sum over internal states, $\sum_j$ is expressed as follows:

$$\sum_j = \sum_{\substack{\text{positions } \boldsymbol{r}_j,\ \text{momenta } \boldsymbol{p}_j,\\ \text{internal energies } \{\epsilon\}}}\,. \tag{4·13}$$

We may now substitute relations (4·11), (4·12) into Eq. (4·9) which takes the form

$$\sum_{kl} \Lambda_{\alpha\beta,kl} M^X_{kl} = -\left(\frac{N}{V}\right)^2 A_{\alpha\beta}\Delta\boldsymbol{r}_\alpha\Delta\boldsymbol{r}_\beta a(\boldsymbol{r}_\alpha, \boldsymbol{r}_\beta, \boldsymbol{p}_\alpha, \boldsymbol{p}_\beta, \{\epsilon\}) \tag{4·14}$$

with

$$a = O(1)\,. \tag{4·15}$$

The important point now is that the sums over states in the definition (4·10) of Λ *cannot* introduce volume factors. Indeed, the presence of the transition probabilities $A_{\alpha j}$ etc. in front of the factors $\overline{X}_j$ etc. implies that, effectively, these sums extend only over a small coherence region much smaller than the size of the system. Thus the operator Λ itself is of order 1, or more precisely of the same order as $A_{\alpha\beta}$ and the solution of Eq. (4·14) can be written in the form

$$M^X_{\alpha\beta} = \left(\frac{N}{V}\right)^2 b(\boldsymbol{r}_\alpha, \boldsymbol{r}_\beta, \boldsymbol{p}_\alpha, \boldsymbol{p}_\beta, \{\epsilon\})\,\Delta\boldsymbol{r}_\alpha\Delta\boldsymbol{r}_\beta\,, \tag{4·16}$$

where

$$b = \Lambda^{-1}a = O(1)\,. \tag{4·17}$$

This result is a direct consequence of the *local* character of Eq. (4·14) or (4·7). If on the contrary the assumption of a homogeneous fluctuation adopted by Kuramoto had been made, one would have the completely different result:

$$M^X_{\alpha\beta} = \frac{1}{N}\left(\frac{N}{V}\right)^2 \times O(1) = \frac{N}{V^2}\times O(1)\,. \tag{4·18}$$

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The final step is to calculate the contribution of $M_{\alpha\beta}^{X}$ to the quadratic fluctuation of the macroscopic variable X:

$$\overline{\delta X^2} = \overline{(\sum_{\alpha} \delta X_\alpha)^2} = \sum_{\alpha} \overline{\delta X_\alpha^2} + \sum_{\alpha \neq \beta} \overline{\delta X_\alpha \delta X_\beta}$$
$$= \overline{X} + \sum_{\alpha \neq \beta} M_{\alpha\beta}^{X} . \tag{4·19}$$

For the reasons explained above, the double sum over states in (4·19) *cannot* yield two volume factors. The cross-correlation $M_{\alpha\beta}^{X}$ is only nonvanishing as long as the corresponding degrees of freedom can interact, i.e., as long as the two colliding particles are nearby. Thus, in the notation of (4·13),

$$\sum_{\alpha \neq \beta} M_{\alpha\beta}^{X} = n^2 \sum_{\boldsymbol{r}_\alpha, \boldsymbol{r}_\beta} \sum_{\boldsymbol{p}_\alpha, \boldsymbol{p}_\beta, \{\epsilon\}} b(\boldsymbol{r}_\alpha, \boldsymbol{r}_\beta, \boldsymbol{p}_\alpha, \boldsymbol{p}_\beta, \{\epsilon\}) . \tag{4·20}$$

In a system which is macroscopically uniform one can integrate over the center-of-mass coordinates:

$$\sum_{\alpha \neq \beta} M_{\alpha\beta}^{X} = n^2 V \sum_{\boldsymbol{r}_\alpha - \boldsymbol{r}_\beta, \boldsymbol{p}_\alpha, \boldsymbol{p}_\beta, \{\epsilon\}} b(\boldsymbol{r}_\alpha - \boldsymbol{r}_\beta, \boldsymbol{p}_\alpha, \boldsymbol{p}_\beta, \{\epsilon\})$$
$$= \left(\frac{N}{V}\right)^2 V \times O(1) . \tag{4·21}$$

Combining with (4·19) we finally obtain

$$\overline{\delta X^2} = \overline{X}[1 + n \times O(1)] \tag{4·22}$$

in agreement with the conjecture made previously by Prigogine and Nicolis. In contrast, if the estimate (4·18) were made, one would obtain

$$\sum_{\alpha \neq \beta} M_{\alpha\beta}^{X} = \frac{N}{V^2} \times \sum_{\boldsymbol{r}_\alpha, \boldsymbol{r}_\beta, \boldsymbol{p}_\alpha, \boldsymbol{p}_\beta, \{\epsilon\}} (\text{const}) = N \times O(1) . \tag{4·23}$$

This latter procedure has been followed by Kuramoto. Let us emphasize again that treating $M_{\alpha\beta}^{X}$ as constant throughout the system is opposite to the very meaning of fluctuation theory. For instance, in the theory of fluctuations in closed systems it is essential to consider a small part of the total volume and evaluate the fluctuations therein, since quite obviously the number of particle fluctuations in the total volume vanish.[7] Incidentally we find here one more serious deficiency of the birth and death formalism which by construction discards the local character of fluctuations. Again, for large scale fluctuations the local aspects become less important and the birth and death formalism can again be used with confidence.

Finally, it is instructive to point out the striking similarity between Eq. (4·7) or (4·9) and the statistical mechanical BBGKY hierarchy for the correlation functions. Let $f_1(1)$ and $f_2(1, 2)$ be respectively the single and the two particle distribution functions of a many-body system. The pair correlation function g_2 is defined by

$$g_2(1, 2) = f_2(1, 2) - f_1(1) f_1(2) , \tag{4·24}$$

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where (1, 2) stand formally for the degrees of freedom of particles 1 and 2. It can be shown that if triple correlations are neglected g_2 obeys the equation[8]

$$\frac{\partial g_2}{\partial t}+L_{12}g_2(1,2)+\mathcal{CV}g_2(1,2)+\theta_{12}f_1(1)f_1(2)=0\,. \tag{4·25}$$

In this relation L_{12}, θ_{12} are operators depending on the interaction potential and acting on the two particle coordinates and momenta; and $\mathcal{CV}$ is an integral operator (the sum of two Vlassov operators[8]) containing $\theta_{12}f_1(2)$ or $\theta_{12}f_1(1)$ as kernel. Comparing with (4·7) or (4·9) we easily establish the correspondence:

$$\begin{aligned}
&g_2(1,2) && \leftrightarrow && M^{X}_{\alpha\beta}\,,\\
&f_1(1) && \leftrightarrow && \overline{X}_\alpha\,,\\
&L_{12} && \leftrightarrow && A_{\alpha\beta}+\sum_j (A_{\alpha j}+A_{\beta j})\overline{X}_j\,,\\
&\mathcal{CV}g_2(1,2) && \leftrightarrow && \sum_{j\neq\beta} A_{\beta j}\overline{X}_\beta M^{X}_{j\alpha}+\sum_{j\neq\alpha} A_{\alpha j}\overline{X}_\alpha M^{X}_{j\beta}\,,\\
&\theta_{12}f_1(1)f_1(2) && \leftrightarrow && A_{\alpha\beta}[M^{X}_{\alpha\alpha}\overline{X}_\beta+M^{X}_{\beta\beta}\overline{X}_\alpha-\overline{X}_\alpha\overline{X}_\beta]\,.
\end{aligned} \tag{4·26}$$

From this analogy and from the well-known results of statistical mechanics it should already be clear that the cross-correlation $M^{X}_{\alpha\beta}$ contains an additional density factor compared to $M^{X}_{\alpha\alpha}$ or to $\overline{X}_\alpha$. As we showed earlier in this subsection, this property is also a rigorous consequence of the structure of the second moment phase space equations (4·7) or (4·9).

§ 5. Concluding remarks

We have defined here a *class of systems* where the fluctuations obey a generalized Einstein formula to a first approximation. The crucial feature of this class was the condition $A_{\alpha\beta}\to 0$ as the distance $|\boldsymbol{r}_\alpha-\boldsymbol{r}_\beta|$ exceeds a suitable coherence length. This condition, which is to be contrasted with Kuramoto's assumption of constant transition probabilities, has required, in turn, a *local description* of the fluctuations by means of a phase space master equation. Clearly, this description is in agreement with the requirements developed in § 2. Indeed, the excess entropy $\delta^2 S(\{X_\alpha\})$ which now becomes a functional of $\boldsymbol{r}$ through $\{X_\alpha\}$ takes the form

$$\delta^2 S(\boldsymbol{r})=\sum_{\alpha\beta}\sum_{\boldsymbol{r}'\boldsymbol{r}''} g_{\boldsymbol{r}'\boldsymbol{r}''}\delta X_\alpha(\boldsymbol{r}')\delta X_\beta(\boldsymbol{r}'') \tag{5·1}$$

with

$$g_{\boldsymbol{r}'\boldsymbol{r}''}\simeq\delta(\boldsymbol{r}'-\boldsymbol{r}'')\,,$$

where the indices α,β do not include now the center of mass coordinate. Thus, the probability distribution

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$$P(\{\delta X_\alpha\}) \propto \exp\left[\frac{1}{2k}\sum_{r\epsilon V}(\delta^2 S(\boldsymbol{r}))\right]$$

$$\simeq \exp\left[\frac{1}{2k}\sum_{r\epsilon V}\sum_{\alpha\beta}\delta X_\alpha(\boldsymbol{r})\delta X_\beta(\boldsymbol{r})\right]. \qquad (5\cdot 2)$$

This permits one to define *reduced* probabilities for a subsystem of size ΔV which will remain appreciable provided ΔV is sufficiently small.

What are the implications of these results to the problem of the onset of evolution through fluctuations around a steady state lacking asymptotic stability? We have, on the one hand, the fact that *local fluctuations* (which in their overwhelming majority are of infinitesimal size) are dominated by the generalized Einstein formula and are therefore damped. On the other hand we have the equally well established fact (see § 3 C) that *large scale fluctuations* can only see the average state of the system and *can be amplified* if the macroscopic equations of evolution predict a point of marginal stability. We believe that this quite opposite behavior suggests strongly *a mechanism of nucleation* of the fluctuations triggering the evolution to a new solution beyond instability. In other terms: because the small, local fluctuations are damped, it is essential that there exists a partial volume of the system, of dimensions much larger than the characteristic molecular dimensions but smaller than the total volume of the system, within which the fluctuations add up to a sizable result capable of modifying the macroscopic behavior. In principle this conjecture can be tested by direct solution of the phase space master equations or by numerical "experiments" of the molecular dynamics type. Work in both directions is presently in progress. Some preliminary results based on a simplified formalism are reported in Ref. 9).

Essential for the derivation of the above results have been the conditions that the reacting mixture is not dense and is maintained, on the average, near a local equilibrium regime. It would be very interesting to extend the theory of fluctuations in open systems by relaxing one or both of these restrictions. Some preliminary steps have been undertaken in this direction.

Finally, it is quite clear that the results derived in this paper provide answers to the objections raised by Kuramoto.[8] As we have shown his model discards the local character of fluctuations which is essential for the validity of Einstein-like formulae. Moreover, Kuramoto's objection concerning the compatibility of instabilities with a generalized Einstein formula is accounted for by the nucleation mechanism whose existence was already suggested by Prigogine and Nicolis[1),2)] and it is further supported by the results derived in this paper.

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Appendix

The Volterra-Lotka model

We consider the autocatalytic scheme

$$\begin{aligned} &A+X \overset{k_1}{\rightarrow} 2X, \\ &X+Y \overset{k_2}{\rightarrow} 2Y, \\ &Y+D \overset{k_3}{\rightarrow} E+D. \end{aligned} \tag{A·1}$$

The concentration of A, D, E is maintained constant. The macroscopic equations of evolution of X, Y admit an infinity of periodic solutions around the marginally stable steady state:

$$X_0=\frac{k_3 D}{k_2}, \quad Y_0=\frac{k_1 A}{k_2}. \tag{A·2}$$

The birth and death master equation reads[1),2)]

$$\begin{aligned} \frac{dP(X, Y, t)}{dt} =& A(X-1)P(X-1, Y, t) - AXP(X, Y, t) \\ &+ (X+1)(Y-1)P(X+1, Y-1, t) - XYP(X, Y, t) \\ &+ D(Y+1)P(X, Y+1, t) - DYP(X, Y, t). \end{aligned} \tag{A·3}$$

It has been shown[1),2)] that in the limit of small fluctuations the mean quadratic deviations become

$$\begin{aligned} &\overline{\delta X^2}, \ \overline{\delta Y^2} = \text{increasing function of } t, \\ &\overline{\delta X \delta Y} = \text{oscillatory function of } t. \end{aligned} \tag{A·4}$$

For the reasons explained in §§ 2 and 3, a correct treatment of local fluctuations necessitates a phase space description. The corresponding master equation for (A·1) is, in the notation of § 3:

$$\begin{aligned} \frac{dP(\{X\}, \{Y\}, t)}{dt} =& \sum_{ikl} A_{ikl}[(X_i+1)P(X_i+1, X_k-1, X_l-1, \{X'\}, \{Y\}, t) \\ &- X_i P(X_i, X_k, X_l, \{X'\}, \{Y\}, t)] \\ &+ \sum_{ijkl} B_{ijkl}[(X_i+1)(Y_j+1)P(X_i+1, Y_j+1, Y_k-1, Y_l-1, \{X'\}, \{Y'\}, t) \\ &- X_i Y_j P(X_i, Y_j, Y_k, Y_l, \{X'\}, \{Y'\}, t)] \\ &+ \sum_{i} C_i[(Y_i+1)P(Y_i+1, \{X\}, \{Y'\}, t) \end{aligned}$$

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$$-Y_i P(Y_i, \{X\}, \{Y'\}, t)]$$
$$+\left(\frac{dP(\{X\}, \{Y\}, t)}{dt}\right)_{el}, \qquad (A\cdot 5)$$

where we have set

$$A_{ikl} = \sum_j A_{ijkl}\bar{A}_j ,$$
$$C_i = \sum_{jkl} C_{ijkl}\bar{D}_j . \qquad (A\cdot 6)$$

$A_{ijkl}, B_{ijkl}, C_{ijkl}$ being the transition probabilities per unit time associated with the three steps of (A·1).

The second moment approximation can be worked out quite straightforwardly for this model. The difference with § 4 is that the equations for the various moments are much more complicated owing to the coupling between the two components X and Y. As an example we reproduce hereafter the equation for $M_{\alpha\beta}^{XY}$:

$$\frac{dM_{\alpha\beta}^{XY}}{dt} = M_{\alpha\alpha}^{X}[\sum_{\substack{k\neq\beta\\ l\neq\beta}} (2B_{\alpha k\beta l}\overline{Y}_k - B_{\alpha\beta kl}\overline{Y}_\beta) + 2\sum_{l\neq\beta} B_{\alpha l\beta\beta}\overline{Y}_l + B_{\alpha\beta\beta\beta}\overline{Y}_\beta]$$
$$- M_{\beta\beta}^{Y}[\sum_{\substack{k\neq\beta\\ l\neq\beta}} B_{\alpha\beta kl}\overline{X}_\alpha + 2\sum_{l\neq\beta} B_{\alpha\beta\beta l}\overline{X}_\alpha + B_{\alpha\beta\beta\beta}\overline{X}_\alpha]$$
$$- M_{\alpha\beta}^{XY}[\sum_{\substack{j\neq\beta\\ k\neq\beta,\, i\neq\beta}} B_{\alpha jkl}\overline{Y}_j + \sum_{\substack{j\neq\alpha\\ k\neq\beta,\, l\neq\beta}} B_{j\beta kl}\overline{X}_j$$
$$+ \sum_{\substack{k\neq\beta\\ l\neq\beta}} (2B_{\alpha k\beta l}\overline{Y}_k + B_{\alpha\beta kl}\overline{Y}_\beta + B_{\alpha\beta kl}\overline{X}_\alpha - B_{\alpha\beta kl}) + \sum_{\substack{k\neq\alpha\\ l\neq\alpha}} A_{\alpha kl}$$
$$+ \sum_{l\neq\beta} (B_{\alpha l\beta\beta}\overline{Y}_l - B_{l\beta\beta\beta}\overline{X}_l + 2B_{\alpha\beta\beta l}\overline{Y}_\beta) + B_{\alpha\beta\beta\beta}\overline{Y}_\beta - B_{\alpha\beta\beta\beta}\overline{X}_\alpha + B_{\alpha\beta\beta\beta} + C_\beta]$$
$$+ 2\sum_{j\neq\beta} M_{\alpha j}^{XY}[\sum_{\substack{k\neq\alpha\\ l\neq\beta}} B_{kj\beta l}\overline{X}_k + \sum_{k\neq\alpha} (B_{kj\beta\beta}\overline{X}_k + B_{\alpha j\beta k}\overline{X}_\alpha - B_{\alpha j\beta k})$$
$$+ B_{\alpha j\beta\beta}\overline{X}_\alpha - B_{\alpha j\beta\beta}] + 2\sum_{j\neq\alpha} M_{j\beta}^{XY}(\sum_{l\neq\alpha} A_{jal} + A_{j\alpha\alpha})$$
$$+ \sum_{j\neq\alpha} M_{\alpha j}^{X}[\sum_{\substack{k\neq\beta\\ l\neq\beta}} (2B_{jk\beta l}\overline{Y}_k - B_{j\beta kl}\overline{Y}_\beta) + 2\sum_{l\neq\beta} B_{jl\beta\beta}\overline{Y}_l + B_{j\beta\beta\beta}\overline{Y}_\beta]$$
$$- \sum_{j\neq\beta} M_{\beta j}^{Y}[\sum_{\substack{k\neq\beta\\ l\neq\beta}} B_{\alpha jkl}\overline{X}_\alpha + 2\sum_{l\neq\beta} B_{\alpha j\beta l}\overline{X}_\alpha + B_{\alpha j\beta\beta}\overline{X}_\alpha]$$
$$+ \sum_{\substack{k\neq\beta\\ l\neq\beta}} (B_{\alpha\beta kl}\overline{X}_\alpha\overline{Y}_\beta - 2B_{\alpha k\beta l}\overline{X}_\alpha\overline{Y}_k) - 2\sum_{l\neq\beta} B_{\alpha l\beta\beta}\overline{X}_\alpha\overline{Y}_l - B_{\alpha\beta\beta\beta}\overline{X}_\alpha\ \overline{Y}_\beta . \qquad (A\cdot 7)$$

All calculations of § 4 can be repeated for Eq. (A·7). The result is that, again, the generalized Einstein formula is recovered consistently for localized fluctuations in spite of the fact that the macroscopic steady state (A·2) lacks asymptotic stability.

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References

1) G. Nicolis and I. Prigogine, Proc. Natl. Acad. Sci. **68** (1971), 2102.
2) G. Nicolis, J. Stat. Phys. **6** (1972), 195.
3) Y. Kuramoto, Prog. Theor. Phys. **49** (1973), 1782.
4) P. Glansdorff and I. Prigogine, *Thermodynamic Theory of Structure, Stability and Fluctuations* (Wiley-Intersience, New York, 1971).
5) G. Nicolis and A. Babloyantz, J. Chem. Phys. **51** (1969), 2632.
6) See, e.g., A. Sommerfeld, *Thermodynamics and Statistical Mechanics* (Academic Press New York, 1964).
7) A. Münster, *Statistical Thermodynamics*, Vol. I (Springer Verlag, Berlin, 1969).
8) M. Baus, Physica **66** (1973), 421.
9) G. Nicolis, M. Malek-Mansour, K. Kitahara and A. Van Nypelseer. Phys. Letters **48A** (1974), 217.

Note 1: This work was completed when we became aware of a preprint by A. Nitzan and J. Ross, entitled "A comment on Fluctuations around Non-Equilibrium Steady States". They show that the factorization assumption of Prigogine and Nicolis is in contradiction with the rigorous maintenance of a local equilibrium distribution throughout the system. Nitzan and Ross objections are answered if one realizes that our analysis deals essentially with the behavior of *localized* fluctuations, whereas in their work Kuramoto and Nitzan and Ross make the assumption of homogeneous fluctuations. We want to express our appreciation to Professor J. Ross for stimulating correspondence on this subject and for communicating to us his paper with Nitzan before publication.

Note 2: This work was submitted for publication when we became aware of a preprint by Y. Kuramoto entitled "Effects of Diffusion on the Fluctuations in Open Chemical Systems". Using a method which appears to be intermediate between the phase space formalism and the method followed in Ref. 9) given in our paper he shows that the extended Einstein formula for the fluctuations is recovered consistently in the limit where the molecules diffuse sufficiently rapidly with respect to the scale characterizing chemical relaxation. Thus, Kuramoto's latest result confirms the original Prigogine-Nicolis theory of fluctuations. Some further results in this field are described in Ref. 9) given in our paper as well as in a forthcoming paper by Malek-Mansour, Nicolis, Van Nypelseer and Kitahara (submitted for publication in Physica).

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