EQUILIBRIUM CONCENTRATION FLUCTUATIONS IN OPEN REACTIVE SYSTEMS

Jack SIMONS[*]

Chemistry Department, University of Utah, Salt Lake City, Utah 84112, USA

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We discuss the calculation of local concentration fluctuations, at constant volume and temperature, for an open, non-interacting, chemically-reactive fluid. One conclusion is that even for ideal mixtures, fluctuations cannot be calculated using a grand-canonical theory if the open volume element constitutes a non-negligible part of the total system. It is also shown that the calculation of equilibrium fluctuations for interacting molecules is, in general, not given by the ordinary grand-canonical result. There does exist a coupling between reaction progress fluctuations and concentration fluctuations due to migration.

In this paper we discuss static concentration fluctuations occurring in open chemically reactive fluids at equilibrium. Intuitively, one might expect concentration fluctuations to arise from either of two sources. Reactant particles can diffuse into or out of an open volume element, thereby altering the local concentrations. In addition, fluctuations in the progress variable of a chemical reaction can affect local concentrations. A question which naturally arises is: how can one incorporate both diffusion and progress variable fluctuations into a calculation of local-concentration fluctuations? Although the present letter does not answer this question, it does show that previously obtained answers are not generally correct.

It should be noted that our goal here is not to investigate the time decay of concentration fluctuations but rather to study *static* fluctuations in an open system which is in equilibrium with a *finite* enclosing volume. Keizer [1] has given a very interesting stochastic treatment of the dynamics of fluctuations for an isomerization reaction in a closed system in the thermodynamic limit ($V \to \infty$). The reader should consult Keizer's article for several other references to this interesting question.

Let us begin by considering a closed vessel of (constant) volume V, which is isolated from its surroundings. We assume that the reversible chemical reaction

$$\nu_1 A_1 + \nu_2 A_2 + \ldots + \nu_s A_s = 0 \tag{1}$$

has reached equilibrium within the vessel, and we designate the equilibrium concentrations of the reactants by $\{C_i^0;\, i = 1, 2, \ldots s\}$. The instantaneous value of the total concentration of reactant i is given in terms of the progress variable[†] ξ as

$$C_i = C_i^0 + \nu_i \xi \,. \tag{2}$$

The stoichiometric coefficients ν_i are positive for products and negative for reactants. The probability of fluctuations in the progress variable, at constant volume and energy (E), can be expressed in terms of the entropy change accompanying the fluctuation [2]

$$P(\xi) = \frac{\exp\{k^{-1}[S(\xi,E,V) - S(0,E,V)]\}}{\int \exp\{k^{-1}[S(\xi,E,V) - S(0,E,V)]\}\mathrm{d}\xi} . \tag{3}$$

Because fluctuations are small, except near critical points, the entropy change appearing in eq. (3) can be accurately approximated as [2]:

$$S(\xi,E,V) - S(0,E,V) = \tfrac{1}{2}(\partial^2 S/\partial \xi^2)_{E,V,\xi=0}\, \xi^2 \,. \tag{4}$$

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[*] Alfred P. Sloan Foundation Fellow.

[†] Notice that one can define a progress variable only for a closed system.

Eq. (3), together with eq. (4), provide the correct probability density for calculating equilibrium average fluctuations of quantities which depend upon ξ.

Let us now turn our attention to a small open subsystem of constant volume Ω, which is in thermal equilibrium with the remainder of the original vessel. The instantaneous concentration of reactant i within the volume Ω is represented by c_i, and the deviation of c_i from its equilibrium value $c_i^0 = C_i^0$ is denoted by δc_i. To calculate equilibrium fluctuations in local concentrations, we propose the following equation*:

$$\langle \delta c_i \delta c_j \rangle^0 = \int \mathrm{d}\xi \, \langle \delta c_i \delta c_j \rangle_\xi P(\xi) \,, \tag{5}$$

where $P(\xi)$ is given by eqs. (3) and (4) and $\langle \delta c_i \delta c_j \rangle_\xi$ is the local-concentration fluctuation calculated at fixed ξ.

Eq. (5) clearly implies that progress variable fluctuations and local concentration fluctuations are not necessarily independent. The concentration fluctuations depend upon the number of molecules of each reactant within Ω, which, in turn, depends upon ξ. Therefore, the progress variable ξ and the number of molecules of each reacting species are interrelated variables. This can also be seen by considering how molecular scattering events give rise to changes in the number of reactant molecules within Ω. Each bimolecular encounter can give rise to one of four distinguishable outcomes:

(i) the molecules non-reactively scatter and remain in Ω;

(ii) the molecules reactively scatter and remain in Ω;

(iii) the molecules non-reactively scatter and one or both of the molecules moves out of Ω;

(iv) the molecules reactively scatter and one or more of the products leaves Ω.

The fourth outcome, whose probability is linked through sum-rules or conservation laws to the probabilities of the first three outcomes, provides the coupling between progress variable- and local concentration-fluctuations.

For non-critical systems, the (symmetric) distribution $P(\xi)$ is quite sharply peaked about $\xi = 0$. In this case, we can evaluate the integral in eq. (5) to a high degree of accuracy by expanding the frozen fluctuation $\langle \delta c_i \delta c_j \rangle_\xi$ in powers of ξ, keeping only terms to second order in ξ. The symmetry and narrowness of $P(\xi)$ allows us to extend the ξ-integration from $-\infty$ to $+\infty$, thereby eliminating the contribution of the term linear in ξ. The equilibrium fluctuations resulting from this expansion are given as follows:

$$\langle \delta c_i \delta c_j \rangle^0 = \langle \delta c_i \delta c_j \rangle_{\xi=0} - \tfrac{1}{2} \left(\frac{\partial^2 \langle \delta c_i \delta c_j \rangle_\xi}{\partial \xi^2} \right)_{E,V,\xi=0} \times \left[\sum_{l,m=1}^{s} \frac{\nu_l \nu_m}{kT} \, \Omega \left(\frac{\partial \mu_l}{\partial n_m} \right)_{T,P,n_{p\neq m}} + \frac{\Delta \bar{V}}{kT} \left(\frac{\partial P}{\partial \xi} \right)_{E,V} - \frac{\Delta \bar{H}}{kT^2} \left(\frac{\partial T}{\partial \xi} \right)_{E,V} \right]^{-1} V^{-1} \,, \tag{6}$$

where we have expressed $(\partial^2 S/\partial \xi^2)_{E,V}$ in terms of the partial molal volume and enthalpy differences ($\Delta \bar{V} = \sum_{i=1}^{s} \nu_i \bar{V}_i$, $\Delta \bar{H} = \sum_{i=1}^{s} \nu_i \bar{H}_i$) and various thermodynamic derivatives. In the $V \to \infty$ (Ω = constant) limit, the equilibrium fluctuations can be seen to reduce to the frozen (at $\xi = 0$) fluctuations. This is the usual result for a grand-canonical ensemble [3], which is valid for non-ideal systems as well. On the other hand, if the ratio Ω/V is not negligibly small, both terms in eq. (6) must be examined more carefully†.

If the molecules in the system are non-interacting, one can use a simple statistical weighting factor to calculate the probability of finding n_i molecules of species i ($i = 1, 2, \ldots s$) in the volume Ω and the remaining $[V(C_i^0 + \nu_i \xi) - n_i] (\equiv N_i - n_i)$ molecules in the volume outside Ω. The proper weighting factor is given by

$$P(n_1, \ldots n_s) = \prod_{i=1}^{s} \frac{N_i!}{(N_i - n_i)! \, n_i!} \left(\frac{\Omega}{V} \right)^{n_i} \left(1 - \frac{\Omega}{V} \right)^{N_i - n_i} . \tag{7}$$

With the above probability function, one obtains the following results for the fluctuations appearing in eq. (5):

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* The superscript 0 is used to designate equilibrium. Eq. (5) is merely a statement of conditional probability. That is, we take the probability $P(\xi)$ of a fluctuation in ξ multiplied by the concentration fluctuation $\langle \delta c_i \delta c_j \rangle_\xi$ occurring at that value of ξ. The result is then averaged over ξ.

† Of course, the grand-canonical ensemble fluctuation theory assumes, from the beginning, that Ω/V is negligible.

$$\langle \delta c_i \delta c_j \rangle_\xi = 0 \qquad \text{if } i \neq j\,, \tag{8a}$$

$$\langle \delta c_i^2 \rangle_\xi = (C_i^0 + \nu_i \xi)(\Omega^{-1} - V^{-1})\,. \tag{8b}$$

The fact that $\langle \delta c_i^2 \rangle_\xi$ is linear in ξ immediately implies that the second term in eq. (6) does not contribute to the overall concentration fluctuations.

We therefore find that, for non-interacting molecules with finite Ω/V, the results of eqs. (8a) and (8b) with $\xi = 0$ give the desired equilibrium fluctuations. It should be pointed out that eq. (8b) is not identical to the usual grand-canonical formula for non-interacting molecules, which states that

$$\langle \delta c_i^2 \rangle^0 = C_i^0 \Omega^{-1}\,. \tag{9}$$

The two results differ by a factor of $1 - \Omega/V$, which reduces to unity only in the $V \to \infty$ limit. Thus, even for ideal reacting mixtures, this correction to the grand-canonical formula should be included.

For non-ideal systems with finite Ω/V, one must compute both terms in eq. (6). The second term can be interpreted as giving rise to a coupling between ξ-fluctuations and concentration fluctuations which are due to diffusion. Thus far, we have been unable to obtain closed expressions for these terms for any model system which might be of general interest. The principal difficulty lies in the fact that the volume $(V-\Omega)$ of the "bath" system cannot be taken to be infinitely large. Until an analytical solution of this problem becomes available, it is our feeling that it would be very useful to compare the results of computer experiments in which $\langle \delta c_i \delta c_j \rangle_{\xi=0}$ and $(\partial^2 \langle \delta c_i \delta c_j \rangle_\xi / \partial \xi^2)_{E,V,\xi=0}$ are obtained for interacting finite systems to the results of the $(V \to \infty)$ grand-canonical theory

$$\langle \delta c_i \delta c_j \rangle = kT\Omega^{-1} (\partial c_i / \partial \mu_j)_{T,\Omega,\mu_{k \neq j}}\,. \tag{10}$$

In this way, one could learn under what conditions corrections to the grand-canonical results due to the non-ideal nature of the system can be neglected. We strongly urge researchers who have the expertise and facilities for such computer studies to undertake these investigations in the near future.

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References

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[2] L.D. Landau and E.M. Lifshitz, Statistical physics (Addison-Wesley, Reading, 1969).

[3] T.L. Hill, Statistical mechanics (McGraw-Hill, New York, 1956).