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Fluctuation-Dissipation Theorem for Chemical Reactions near a Critical Point

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In a fluid mixture near a critical point, there are long-range fluctuations in the component concentrations that exceed the range of the intermolecular forces. If the components are linked by a chemical reaction, then the fluctuations in the concentrations of the reactants and products have their origin in the fluctuation in the extent of reaction, ξ. The fluctuation in ξ about the position of chemical equilibrium can be expressed by the statistical variance, var(ξ_e), where the subscript "e" denotes equilibrium. We show that var(ξ_e) is inversely proportional to $(\partial\Delta G/\partial\xi)_e$, where ΔG is the Gibbs energy difference separating products from reactants. Because the relaxation time, τ, that governs the rate of approach of the reaction to equilibrium is also inversely proportional to $(\partial\Delta G/\partial\xi)_e$, τ is proportional to var(ξ_e). This latter relation constitutes a fluctuation-dissipation theorem. Under circumstances near a critical point where var(ξ_e) → ∞, the theorem predicts that the specific relaxation rate $^1/_\tau$ should go to zero and that the rate of approach of the reaction to chemical equilibrium should slow.

I. Introduction

In a fluid mixture near a liquid−vapor or liquid−liquid critical point, there are long-range fluctuations in composition that do not occur elsewhere in the phase diagram.[1] When the temperature, T, is close enough to the critical temperature, T_C, the spatial extent of these fluctuations exceeds the range of the intermolecular forces. In this situation, the macroscopic properties of the fluid are dominated by the fluctuations and become largely independent of the intermolecular forces. This phenomenon is the basis for applying the principle of universality to critical effects in fluid mixtures.[2,3]

In the case of a chemically reacting fluid, the fluctuations in the concentrations of the reactants and products have their origin in the fluctuations in the extent of reaction. We will show that the variance of the statistical distribution of the extent of reaction, ξ, about its equilibrium value, ξ_e is inversely proportional to the thermodynamic derivative, $(\partial\Delta G/\partial\xi)_e$, where ΔG is the Gibbs energy difference separating products from reactants and the subscript on the derivative indicates that it has been evaluated at $\xi = \xi_e$. Because the specific rate, $^1/_\tau$, of relaxation of the reactant and product concentrations toward equilibrium is proportional to $(\partial\Delta G/\partial\xi)_e$, the value of τ is ultimately determined by the extent of the fluctuations about equilibrium. This connection constitutes a fluctuation-dissipation theorem, which should find application in the case of chemically reacting mixtures near a critical point, where such fluctuations are extreme.

II. Theory

We consider a reaction that converts reactants 1 and 2 to products 3 and 4:

$$\nu_1(1) + \nu_2(2) \rightarrow \nu_3(3) + \nu_4(4) \qquad (1)$$

where the ν_j's ($j = 1-4$) are stoichiometric coefficients. The molar concentrations, c_j, of the reactants and products are linked to the extent of reaction by the equation

$$c_j = c_j(0) \pm \nu_j\xi \qquad (2)$$

where the $c_j(0)$'s are the initial concentrations. The plus sign in eq 2 applies to products, and the minus sign applies to reactants.

We let $Q(T, V, \{c_j\})$ be the canonical partition function, where T is the absolute temperature and V is the volume of the fluid. The set of molar concentration variables $\{c_j\}$ includes all components, both reactive and inert. If we let μ_j be the chemical potential per mole of the jth component, then following Ben-Naim[4] the grand canonical partition function $\Xi(T, V, \{\mu_j\})$ is given by the sum

$$\Xi(T, V, \{\mu_j\}) = \sum_{\{c_j\}} Q(T, V, \{c_j\}) \exp(\beta V \sum_k c_k \mu_k) \qquad (3)$$

where $\beta = (k_B T)^{-1}$ and k_B is Boltzmann's constant. The variance in the concentration of the jth component is defined by

$$\mathrm{var}(c_j) = \langle c_j^2 \rangle - \langle c_j \rangle^2 \qquad (4)$$

The nth moment of the statistical distribution of the values of c_j is computed from the grand partition function using

$$\langle c_j^n \rangle = (\Xi)^{-1} \sum_{\{c_m\}} c_j^n Q(T, V, \{c_m\}) \exp(\beta V \sum_k c_k \mu_k) \qquad (5)$$

Setting $n = 1$ in eq 5 and differentiating eq 3 with respect to μ_j, we obtain

$$\langle c_j \rangle = \frac{1}{\beta V} \frac{1}{\Xi} \frac{\partial \Xi}{\partial \mu_j} \qquad (6)$$

Setting $n = 2$, we obtain

$$\langle c_j^2 \rangle = \frac{1}{(\beta V)^2} \frac{1}{\Xi} \frac{\partial^2 \Xi}{\partial \mu_j^2} \qquad (7)$$

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Introducing the identity[4]

$$\frac{1}{\Xi}\frac{\partial^2\Xi}{\partial\mu_j^{\,2}} = \frac{1}{\Xi}\frac{\partial}{\partial\mu_j}\left(\Xi\frac{\partial \ln \Xi}{\partial\mu_j}\right) \tag{8}$$

into eq 7, we can substitute eq 7 plus eq 6 into eq 4 to obtain

$$\mathrm{var}(c_j) = \frac{1}{(\beta V)^2}\left(\frac{\partial^2 \ln \Xi}{\partial\mu_j^2}\right) \tag{9}$$

Taking note again of eq 6, eq 9 becomes

$$\mathrm{var}(c_j) = \frac{1}{\beta V}\left(\frac{\partial\langle c_j\rangle}{\partial\mu_j}\right) \tag{10}$$

If j refers to one of the species involved in the reaction, then the thermodynamic fluctuations in the value of c_j are determined by the fluctuations in ξ. Substituting eq 2 into eq 4, we obtain

$$\mathrm{var}(c_j) = \nu_j^{\,2}(\langle\xi^2\rangle - \langle\xi\rangle^2) = \nu_j^{\,2}\,\mathrm{var}(\xi) \tag{11}$$

Using

$$\mathrm{d}c_j = \pm\nu_j\,\mathrm{d}\xi \tag{12}$$

$\mathrm{var}(c_j)$ in eq 10 can be expressed as

$$\mathrm{var}(c_j) = \pm\frac{\nu_j}{\beta V}\left(\frac{\partial\langle\xi\rangle}{\partial\mu_j}\right) \tag{13}$$

The Gibbs energy difference separating products from reactants is given by

$$\Delta G = \nu_3\mu_3 + \nu_4\mu_4 - \nu_1\mu_1 - \nu_2\mu_2 \tag{14}$$

We note that the chemical potential of a reactant or product is necessarily a function of $\langle\xi\rangle$, so that the differentiation of eq 14 leads to

$$\frac{\partial\Delta G}{\partial\langle\xi\rangle} = \nu_3\frac{\partial\mu_3}{\partial\langle\xi\rangle} + \nu_4\frac{\partial\mu_4}{\partial\langle\xi\rangle} - \nu_1\frac{\partial\mu_1}{\partial\langle\xi\rangle} - \nu_2\frac{\partial\mu_2}{\partial\langle\xi\rangle} \tag{15}$$

By introducing eq 13, eq 15 becomes

$$\frac{\partial\Delta G}{\partial\langle\xi\rangle} = \frac{1}{\beta V}\sum_{j=1}^{4}\frac{\nu_j^{\,2}}{\mathrm{var}(c_j)} \tag{16}$$

The sum on the right side of eq 16 can be computed using eq 11. Evaluating the result at chemical equilibrium and noting that in the thermodynamics ξ has the sense of $\langle\xi\rangle$ in statistical mechanics, eq 16 can be expressed as

$$\left(\frac{\partial\Delta G}{\partial\xi}\right)_{\mathrm{e}} = \frac{(4/\beta V)}{\mathrm{var}(\xi_{\mathrm{e}})} \tag{17}$$

where ξ_{e} is the equilibrium value of ξ.

Sufficiently close to equilibrium, the time dependence, $\mathrm{d}\xi/\mathrm{d}t$, of the extent of reaction is determined by the equation

$$\frac{\mathrm{d}\xi}{\mathrm{d}t} = -\frac{1}{\tau}(\xi - \xi_{\mathrm{e}}) \tag{18}$$

where $^1/_\tau$ is the specific rate of relaxation, which is given by[5]

$$\frac{1}{\tau} = \frac{r'(\xi_{\mathrm{e}})}{RT}\left(\frac{\partial\Delta G}{\partial\xi}\right)_{\mathrm{e}} \tag{19}$$

In eq 19, R is the gas law constant, and $r'(\xi_{\mathrm{e}})$ is the rate of the forward reaction at equilibrium.[5] Equation 19 follows directly from the Guldberg−Waage law of mass action,[6] but it can also be derived on the basis of the linear response theory.[7]

The next step is to substitute eq 17 into eq 19. We obtain

$$\frac{1}{\tau} = \frac{4r'(\xi_{\mathrm{e}})}{\beta VRT\,\mathrm{var}(\xi_{\mathrm{e}})} \tag{20}$$

Equation 20 is our fluctuation-dissipation theorem.

III. Discussion and Conclusions

The use of the grand canonical ensemble to compute concentration fluctuations has its origin in the Kirkwood−Buff theory of solutions.[8] This method has recently been applied to the analysis of solute−solvent[9,10] and solute−solute[11] molecular clustering in supercritical fluids. The factor of 4 in eq 20 is identical to the number of species involved in eq 1 and will be different for reactions involving differing numbers of species.

To analyze the behavior of $\mathrm{var}(\xi_{\mathrm{e}})$ as $T \to T_{\mathrm{C}}$ in the case of a chemically reacting liquid mixture near its consolute point,[12−14] we focus on eq 17. If $\mathrm{var}(\xi_{\mathrm{e}})$ is to diverge as $T \to T_{\mathrm{C}}$, then $(\partial\Delta G/\partial\xi)_{\mathrm{e}}$ must approach zero. In a homogeneous reacting liquid mixture, this is predicted to occur if the fixed thermodynamic variables are restricted to the temperature T, the pressure P, and no more than one of the concentrations $\{c_j\}$ of the species making up the mixture.[15] Thus, if there is no more than one chemically inert component in the mixture, we can expect $(\partial\Delta G/\partial\xi)_{\mathrm{e}} \to 0$ and $\mathrm{var}(\xi_{\mathrm{e}}) \to \infty$ as $T \to T_{\mathrm{C}}$. By virtue of eq 20, we can also expect $^1/_\tau \to 0$ under these circumstances. This has been observed experimentally in the case of $\mathrm{S_N}1$ hydrolysis[12−14] reactions, at least where T approaches T_{C} from above.[16]

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