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Fluctuations in Multicomponent Solutions and Light Scattering Intensity Revisited

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The fluctuation of physical quantities in multicomponent solutions and its relevance to the light scattering intensity are reexamined. The fluctuation of thermodynamic quantities in solutions is derived without any constraint to the system, such as the assumption of constant volume or constant mass. Based on the mean square correlation among the fluctuation of thermodynamic variables, a general expression for the light scattering intensity is obtained. The present result coincides with that derived by assuming artificial constraints to the volume or the mass of the solutions, the procedure which has been adopted customarily by previous workers. The relation between the fluctuation of density and the mass fraction is also discussed.

The intensity of light scattering is proportional to the mean square of the fluctuation of the dielectric constant of the scattering medium $\langle(\delta\varepsilon)^2\rangle$.[1—6] Since the dielectric constant ε is a function of thermodynamic variables, a number of light scattering measurements were carried out to get insight into the fluctuations in solutions such as the concentration fluctuations and the partial structure of solutions.[7—9]

In order to describe the light scattering intensity in terms of thermodynamic fluctuations, we must know the correlation among the thermodynamic fluctuation in local parts of the solution; this is achieved by considering the change of minimum work of the system upon fluctuation[10,11] as described in textbooks.[1,2,12] However, we should like to draw attention to the point that in all these textbooks one of the extensive variables is fixed in order to derive the correlation among the fluctuations. In the paper by Cohen et al.[13] cited in these textbooks, the authors stated that "to compute minimum work for a system we must define the system by keeping one extensive variable fixed". Accordingly, they derived the fluctuation by fixing the volume or the total mass M (or the total number N) of the system. The latter approach to fix the total mass is followed in most subsequent textbooks.[1,2,12] However, such a constraint is obviously not appropriate for the treatment of the general fluctuation in *local parts* of solution. To explicitly demonstrate the deficiency we consider a binary solution of molecules 1 and 2 of masses m_1 and m_2 and numbers N_1, and N_2. The constraint of the total mass requires $\delta M = m_1\delta N_1 + m_2\delta N_2 = 0$,[1] where δ symbolizes the change in the total mass and the numbers in the *subsystem* in the terminology of thermodynamics. Such a constraint means that when N_1 molecules 1 diffuse into (out of) the subsystem, m_1N_1/m_2 molecules 2 must counterbalancingly diffuse out (in), which is obviously incompatible with the natural fluctuation in local parts of solution.

This incongruity appears to stem partly from the confusion of the previous workers that the scattering volume was the *subsystem* whose volume was determined by the spot size of the laser used for scattering experiments. However, we should like to point out that the fixed scattering volume does not mean a constant volume in the thermodynamic sense since the thermodynamic variable conjugate to volume, that is pressure, does nothing at all to keep the volume constant in this scattering event.

Therefore, a general expression free from any constraint must be derived which leads to the correlation among the fluctuations, and ultimately to the light scattering intensity. This is the primary purpose of the present paper.

Fluctuation in Multicomponent Solutions

First, we summarize the thermodynamics of a subsystem of L-component solutions for the sake of the later discussion. The subsystem is a part of the system which is large enough to allow thermodynamic treatments and yet small enough relative to the total system. The surrounding of the subsystem works as the source and sink of heat, pressure, and particles for the subsystem.

We consider thermodynamic quantities of the subsystem *per unit mass*. The introduction of the variables per unit mass will be shown to be crucial in the calculation of fluctuations. The total mass of the subsystem M is given in terms of the mass m_i and the number N_i of the i-th component as $M = \sum_{i=1}^{L} m_iN_i$. We define also the mass fraction c_i by m_iN_i/M, which satisfies the identity $1 = \sum_{i=1}^{L} c_i$. Then the Gibbs relation, Euler's equation, and the Gibbs–Duhem relation of the subsystem per unit mass are given as

$$\mathrm{d}e = T\mathrm{d}s - P\mathrm{d}v + \sum_{i=1}^{L-1} \mu_i'\mathrm{d}c_i, \tag{1}$$

$$e = Ts - Pv + \sum_{i=1}^{L-1} \mu_i' c_i + \frac{\mu_L}{m_L}, \tag{2}$$

$$0 = s\mathrm{d}T - v\mathrm{d}P + \sum_{i=1}^{L-1} c_i \mathrm{d}\mu_i' + \frac{1}{m_L}\mathrm{d}\mu_L, \tag{3}$$

where e, s, and v represent, respectively, internal energy, entropy, and the volume of the subsystem per unit mass, and T and P represent temperature and pressure of the subsystem, respectively. The chemical potentials μ_i' $(i = 1,2,\cdots,L-1)$ are defined as $\mu_i' = \mu_i/m_i - \mu_L/m_L$ where μ_i is the chemical potential of the i-th component. Due to the identity $1 = \sum_{i=1}^{L} c_i$ among the mass fractions, the above equations are expressed in terms of $L-1$ mass fractions. Note that Eqs. 1, 2, and 3 hold *without* the assumption that the total mass of the subsystem M is constant. That is to say, the equation is valid irrespective of the size of M of the subsystem, so that δM is not required to be zero.

In the case of binary solutions ($L = 2$), we have the identity $1 = c_1 + c_2$. Then, the Gibbs relation in Eq. 1 is simplified as $\mathrm{d}e = T\mathrm{d}s - P\mathrm{d}v + \mu\mathrm{d}c$ where c and μ are the mass fraction of molecule 1 and the chemical potential defined as $c = c_1$ and $\mu = \mu_1/m_1 - \mu_2/m_2$.[14]

Next, we consider fluctuations of thermodynamic quantities in an L-component solution. The probability W of the fluctuation of thermodynamic quantities of the subsystem is given by $W \propto \exp\left[-\frac{\delta R}{k_B T_0}\right]$ where k_B and T_0 are the Boltzmann constant and the temperature of the external system, respectively, and δR is the minimum work of the subsystem near the equilibrium, which is given as $\delta R = \frac{1}{2}\left[\delta S\delta T - \delta V\delta P + \sum_{i=1}^{L}\delta\mu_i\delta N_i\right]$ in terms of $L+2$ conjugate sets of the variables. The symbol δ in the right-hand-side denotes the deviation (or fluctuation) of each quantity from its average. If one assumes a restriction such as $\delta M = 0$ or $\delta V = 0$ as the previous workers did,[1,2,12] the minimum work δR may be a function of only $L+1$ conjugate sets of the thermodynamic variables. Without such restriction, however, we must start from the minimum work, which is a function of L+2 conjugate sets of the variable.

The fluctuation of any extensive variable X can be written in terms of the corresponding variable per unit mass x and the total mass of the subsystem M as $\delta X = x\delta M + M\delta x$. Thus, the minimum work is rewritten in terms of the variables per unit mass as

$$\begin{aligned}\delta R = &\frac{1}{2}M_0\left[\delta T\delta s - \delta P\delta v + \sum_{i=1}^{L-1}\delta\mu_i'\delta c_i\right]\\ &+\frac{1}{2}\delta M\left[s\delta T - v\delta P + \sum_{i=1}^{L-1} c_i\delta\mu_i' + \frac{1}{m_L}\delta\mu_L\right],\end{aligned} \tag{4}$$

where M_0 is the average mass of the subsystem. The second term in Eq. 4, which is proportional to the fluctuation of the total mass δM, becomes null on account of the Gibbs–Duhem relation in Eq. 3. As a result, the minimum work of the L-component solution can be simply written as

$$\delta R = \frac{1}{2}M_0\left[\delta T\delta s - \delta P\delta v + \sum_{i=1}^{L-1}\delta\mu_i'\delta c_i\right]. \tag{5}$$

Equation 5 shows that the minimum work of an L-component solution can now be expressed in terms of $L+1$ sets of variables: (T,s), (P,v), (μ_1',c_1), (μ_2',c_2), $\cdots$, and (μ_{L-1}',c_{L-1}). In the case of binary solutions, the minimum work is simplified as $\delta R = \frac{1}{2}M_0[\delta T\delta s - \delta P\delta v + \delta\mu\delta c]$ where we have used the definition of c and μ given above.

Equation 5 is essentially the same as those derived by previous authors who imposed a restriction such as $\delta M = 0$ or $\delta V = 0$.[1,2,12] Thus, the probabilities of the correlation among the fluctuation of thermodynamic variables obtained in the present work coincide with those derived by the previous workers under the artificial constraints[1,2,12] (see, for example, Eq.(10.C.40) in Ref. 1 for binary solutions). However, the difference is that they assumed a constraint such as constant mass in the derivation of the minimum work, which is in diametrical contrast to the present derivation attained with no constraint. To be more explicit, since the previous workers assumed that $\delta M = 0$, the second term in Eq. 4 vanished by this artificial enforcement, whereas the term vanishes automatically by virtue of the Gibbs–Duhem relation in Eq. 3 as mentioned above. On account of the above coincidence the expression of the fluctuation in the textbooks cited[1,2,12] can be used safely for any ensembles.

Light Scattering Intensity of Binary Solutions

In this section we relate the light scattering intensity of binary solutions to the fluctuation of the thermodynamic quantities considered in the preceding section. Since we should like to make our theory as general as possible, we start by considering the fluctuation of the dielectric constant $\delta\varepsilon$ as a function of the fluctuation of the full four variables T, P, N_1, and N_2. By using the mass fraction c and the total mass of the subsystem M, the fluctuation of the dielectric constant can be written as

$$\begin{aligned}\delta\varepsilon = \left(\frac{\partial\varepsilon}{\partial P}\right)_{T,c,M}\delta P + \left(\frac{\partial\varepsilon}{\partial T}\right)_{P,c,M}\delta T + \left(\frac{\partial\varepsilon}{\partial c}\right)_{P,T,M}\delta c&\\ +\left(\frac{\partial\varepsilon}{\partial M}\right)_{P,T,c}\delta M.&\end{aligned} \tag{6}$$

Since the dielectric constant is an intensive variable, the equation $\left(\frac{\partial\varepsilon}{\partial M}\right)_{P,T,c} = 0$ must hold intrinsically. Thus, the last term in the right-hand-side of Eq. 6 vanishes to leave the fluctuation of dielectric constant as a function of only three variables, P, T, and c as

$$\delta\varepsilon = \left(\frac{\partial\varepsilon}{\partial P}\right)_{T,c}\delta P + \left(\frac{\partial\varepsilon}{\partial T}\right)_{P,c}\delta T + \left(\frac{\partial\varepsilon}{\partial c}\right)_{T,P}\delta c.$$

Referring to the correlation among the fluctuation of thermodynamic variables, we have the mean square of the fluctuation of the dielectric constant as

$$\left\langle(\delta\varepsilon)^2\right\rangle = \left(\frac{\partial\varepsilon}{\partial P}\right)_{s,c}^2\left\langle(\delta P)^2\right\rangle + \left(\frac{\partial\varepsilon}{\partial T}\right)_{P,c}^2\frac{k_B T_0^2}{C_P} + \left(\frac{\partial\varepsilon}{\partial c}\right)_{T,P}^2\left\langle(\delta c)^2\right\rangle, \tag{7}$$

where C_P is the heat capacity at constant pressure defined as $C_P = M_0 T_0\left(\frac{\partial s}{\partial T}\right)_{P,c}$. Equation 7 is the same as that in the textbooks,[1,2,12] but since we do not assume any constraint, the ensemble is more general than that considered by the previous workers. Thus, Eq. 7 can be applied for average values in any kind of ensembles. The first term of Eq. 7 originates from the adiabatic pressure fluctuation, so that it must correspond to the Brillouin scattering. The remaining two terms are associated with the fluctuation in temperature and the mass fraction, so they correspond to the Rayleigh scattering.

We should like to repeat that the last term in Eq. 6 vanishes intrinsically because the dielectric constant is an intensive variable. This point is fundamentally different from the result obtained by imposing the artificial constraint of $\delta M = 0$ as in the previous works.[1,2,12] The extension of Eq. 7 from binary to multicomponent solutions is straightforward.

Density Fluctuations in Binary Solutions

So far we have discussed the effect of the fluctuation of the mass fraction upon the light scattering intensity in binary solutions. Since we allow free diffusion across the boundary of the subsystem, the fluctuation of density of the subsystem can take place, which also contributes to the light scattering intensity. In this section we examine the relation between the fluctuation of the density and the concentration in binary solutions, which is not given explicitly in previous textbooks.

Since the density of the binary solution ρ is equal to the inverse of the volume per unit mass v ($\rho = 1/v$), it is more convenient to choose the set of v, T, and c than the set of P, T, and c as the thermodynamic variables. Then, the minimum work corresponding to Eq. 5 becomes

$$\delta R = \frac{1}{2}M_0 \left[\left(\frac{\partial s}{\partial T}\right)_{v,c} (\delta T)^2 - \left(\frac{\partial P}{\partial v}\right)_{T,c} \left[\delta v - \left(\frac{\partial v}{\partial c}\right)_{T,P} \delta c\right]^2 + \left(\frac{\partial \mu}{\partial c}\right)_{T,P} (\delta c)^2 \right]. \tag{8}$$

Note that Eq. 8 can be derived without assuming any constraint in the subsystem. Then, the averages of the correlation of the fluctuation of ρ, T, and c are obtained as

$$\langle(\delta T \delta c)\rangle = \langle(\delta T \delta \rho)\rangle = 0, \tag{9}$$

$$\langle(\delta \rho \delta c)\rangle = \left(\frac{\partial \rho}{\partial c}\right)_{T,P} \left\langle(\delta c)^2\right\rangle, \tag{10}$$

$$\left\langle(\delta \rho)^2\right\rangle = \rho_0^2 \left(\frac{\partial \rho}{\partial P}\right)_{T,c} \frac{k_B T_0}{M_0} + \left(\frac{\partial \rho}{\partial c}\right)^2_{T,P} \left\langle(\delta c)^2\right\rangle, \tag{11}$$

where ρ_0 is the average density of the subsystem. Equations 9 and 10 show that a density fluctuation does not correlate to a fluctuation of temperature, but does correlate to the fluctuation of the mass fraction. Equation 11 gives the relation between the fluctuations of the density and the mass fraction. The first and the second term in the right hand side of Eq. 11 correspond to the fluctuation induced by the pressure and by the concentration fluctuation, respectively. Thus, the density fluctuation can be obtained experimentally through Eq. 11 in connection with the fluctuation of the mass fraction.

Conclusion

In this paper we have derived the general expressions for the fluctuation in binary solutions without imposing any artificial constraints. The obtained expressions are the same as those derived previously, but we maintain that the present derivation is on a physically more sound basis. The present derivation guarantees the expression in textbooks, despite the imperfection in their derivation. During the course of the present work we have noticed that little attention has been given to the importance of the Gibbs–Duhem relation in Eq. 3 in deriving the correlation of thermodynamic fluctuations.

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