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Scaled Structure Function in Phase Separation Process

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For a quenched, unstable system of off-critical liquid mixture, the dynamical scaling law is discussed. A simple method to compute the scaled form of the structure function is given by assuming a screened pair distribution function of droplets.

It has been revealed that a dynamical scaling law exists in the process of phase separation. The scaling properties seem to depend on systems. Here we restrict our interest to the middle stage of an off-critical liquid mixture with a low concentration, where we may apply the droplet-fusion picture. For a spherical droplet system with order parameter $s=1$ (in droplet) and $s=0$ (in background), the structure function is given by

$$S(\boldsymbol{q}, t)=\int_0^\infty dv n(v, t)v^2\Psi(Rq)^2 - \int_0^\infty dv_1\int_0^\infty dv_2 n(v_1, t)n(v_2, t) \times v_1\Psi(R_1q)v_2\Psi(R_2q) \times\int d^3\boldsymbol{r}e^{i\boldsymbol{q}\cdot\boldsymbol{r}}[1-W(v_1, v_2; \boldsymbol{r}, t)], \quad (1)$$

where $n(v, t)$ is the number density of droplets of volume $v=4\pi R^3/3$, $\Psi(Rq)$ the structure factor of a single droplet defined by $\Psi(Q)=3(\sin Q - Q\cos Q)/Q^3$. $W(v_1, v_2; \boldsymbol{r}, t)$ is the pair distribution function of droplets with volume v_1, v_2 ($v_i=4\pi R_i^3/3$) normalized as $W(v_1, v_2; \boldsymbol{r}, t)=1$ for $r\to\infty$, where $\boldsymbol{r}$ is the distance between the centers of droplets. Note that an exclusion condition $W(v_1, v_2; \boldsymbol{r}, t)=0$ for $r\leqq R_1+R_2$ is necessary to derive this formula and to assure the sum-rule

$$\frac{1}{(2\pi)^3}\int d^3\boldsymbol{q}S(\boldsymbol{q}, t)=\phi(1-\phi), \quad (2)$$

where ϕ is the volume fraction of minor phase defined by

$$\phi=\int_0^\infty dv\, vn(v, t)=\bar{s}. \quad (3)$$

In the stage dominated by the droplet-fusion process, we may employ Smoluchowski's equation[1] for $n(v, t)$:

$$\frac{\partial}{\partial t}n(v, t)=-n(v, t)\int_0^\infty K(v, v')n(v', t)dv' + \frac{1}{2}\int_0^v K(v', v-v') \times n(v', t)n(v-v', t)dv'. \quad (4)$$

The collision frequency is given by

$$K(v, v')=4\pi[D(v)+D(v')](R+R'), \quad (5)$$

where $D(v)$ is the diffusion constant of droplet of volume $v=4\pi R^3/3$. This formula is derived by equating $K(v, v')$ to the steady state flow of the mutual diffusion equation

$$\partial W(v, v'; \boldsymbol{r}, t)/\partial t =[D(v)+D(v')]\nabla^2 W(v, v'; \boldsymbol{r}, t) \quad (6)$$

with boundary conditions $W(R+R')=0$ (absorptive core) and $W(\infty)=1$. It has been shown that if $D(v)$ obeys a power law $D(v)\propto R^{-\lambda}$, Smoluchowski's equation has an asymptotic scaling solution[2,3]

$$n(v, t)=[\bar{n}(t)/\bar{v}(t)]\Phi(v/\bar{v}(t)), \quad (7)$$

where

$$\bar{n}(t)=\int_0^\infty dv\, n(v, t), \quad (8)$$

and $\bar{v}(t)=\phi/\bar{n}(t)$, which obeys a power law $\bar{v}(t)\propto t^{3/(\lambda+2)}$.

For a liquid mixture one has $\lambda=1$, i.e., Stokes law $D(v)=A/R$, where $A=kT/5\pi\eta$ if the viscosity η in droplets is equal to that in background, then one finds $\bar{v}(t)\propto t$, i.e., the mean radius of

Table. I. Moments $\langle\rho^m\rangle$ defined by Eq. (18) and related quantities.

m	Ref. 2)*)	exp$(-u)$**)
$-1(=b)$	1.250	1.354117
0	1.0	1.0
$1(=a)$	0.915	0.892980
2	0.931	0.902745
3	1.027	1.0
4	1.214	1.190639
5	1.517	1.504575
6	1.990	2.0
$1+ab$	2.145	2.209199
ϕ_c	0.132	0.135608

*)Ohta's interpolation formula[6] is used.
**)$\langle\rho^m\rangle$ is given by Gamma function $\Gamma(1+m/3)$.

droplets grows as $t^{1/3}$. Friedlander and Wang[2] calculated the scaling function $\Phi(u)$ numerically. Here we approximate it by e^{-u} to simplify the following analysis. This form is the scaling solution for the constant collision frequency, and as is shown in Table I this approximation is not so bad for the practical purposes.

In the scaling region one finds

$$d\bar{n}/dt=-4\pi A(1+ab)\bar{n}^2\,, \tag{9}$$

where

$$\left.\begin{matrix}a\\ b\end{matrix}\right\}=\int_0^\infty u^{\pm 1/3}\Phi(u)du\,. \tag{10}$$

By using Eq. (9) one may define the mean-life-time of droplets by $\tau_l^{-1}=4\pi A(1+ab)\bar{n}$, and the mean-free-path by $\lambda=(D(\bar{v})\tau_l)^{1/2}$, i.e.,

$$\lambda\cong 0.39\phi^{-1/2}\bar{R}\,, \tag{11}$$

where $\bar{R}=(3\bar{v}/4\pi)^{1/3}$ and the numerical result in Table I is used. Equation (11) with a criterion $\lambda>\bar{R}$ indicates a rough upper-bound $\phi_c\cong 0.15$ for the validity of the present droplet kinetic model. On the other hand, Eq. (9) can be rewritten as

$$d\bar{v}/dt=4\pi A(1+ab)\phi\,. \tag{12}$$

For the condensation-evaporation process[4] it has been found that $\bar{v}(t)$ is also proportional to t, but the rate does not depend on ϕ. Then the lower bound $\phi^*\cong 0.010$ is estimated with the use of the classical value $c_0=1/6$ for the universal constant. This result is consistent with Siggia's[5] but smaller than Ohta's[6] estimation $\phi^*\cong 0.021$ by half.

The next problem is to give a resonable form of the pair distribution function $W(v, v'; \boldsymbol{r}, t)$ in Eq. (1). Near a droplet $W(\boldsymbol{r}, t)$ should be reduced by the fusion-effect, i.e., the absorptive-core. For small ϕ we have

$$W(v, v'; \boldsymbol{r})=\begin{cases}0 & \text{for } r\leqq R+R'\,,\\ 1-(R+R')/r & \\ & \text{for } r>R+R'\,,\end{cases} \tag{13}$$

i.e., the steady state solution of the mutual-diffusion equation (6) with absorptive-core condition. The absorptive effect will be shielded when the concentration ϕ is increased. Rikvold and Gunton[7] assumed a kind of step function with an exclusion volume which is determined selfconsistently by conservation-law

$$S(\boldsymbol{q}\to 0, t)=0\,. \tag{14}$$

In their theory the upper-bound $\phi_c(=0.125$ for mono-dispersive case) is included, i.e., the exclusion radius R_e must not be smaller than $R+R'$, as is noted below Eq. (1). For small ϕ the reduction is too strong compared with Eq. (13). As a result the characteristic length is found to be proportional to $\phi^{-1/3}\bar{R}$ which is the mean-distance between droplets. Ohta[6] has solved a diffusion-reaction equation neglecting the v, v'-dependence of $W(v, v'; \boldsymbol{r}, t)$ and introducing an external factor to ensure the conservation condition (14). He found a characteristic length $\phi^{-1/2}\bar{R}$ which is consistent with the mean-free-path λ given by Eq. (11). But in his theory the sum-rule (2) is not ensured because $W(v, v'; \boldsymbol{r})$ should have, at least, the v, v'-dependence of exclusion radius $R+R'$. Thus the upper-bound ϕ_c is not included in his theory. Here let us employ another phenomenological form of $W(\boldsymbol{r}, t)$: Assume the same scaling-length $\bar{R}(t)$ for $W(\boldsymbol{r}, t)$ and modify the small ϕ solution (13) by exponential-screening, i.e.,

$$W(v, v'; \boldsymbol{r}, t)=\mathcal{W}(r/(R+R'))\,,$$

$$\mathcal{W}(x)=\begin{cases}0 & \text{for } x\leqq 1\,,\\ 1-e^{-K(x-1)}/x & \text{for } x>1\,,\end{cases} \tag{15}$$

where screening parameter K is determined with

the use of the conservation-condition (14) by

$$3(1+K)/K^2=\phi_c/\phi-1\,, \tag{16}$$

where

$$\phi_c=1/2[\langle\rho^3\rangle+3\langle\rho^4\rangle\langle\rho^5\rangle/\langle\rho^6\rangle] \tag{17}$$

and

$$\langle\rho^m\rangle=\int_0^\infty \rho^m \Phi(\rho^3)3\rho^2 d\rho\,. \tag{18}$$

For the approximation $\Phi(u)=e^{-u}$, one obtains $\phi_c=0.1356\cdots$, which is the upper-bound because $K\to\infty$ with $\phi\to\phi_c$. On the other hand, for small ϕ one finds that $K=(3\phi/\phi_c)^{1/2}$, i.e., the screening length is given by $\xi=2\bar{R}K^{-1}\cong 0.41\ \phi^{-1/2}\bar{R}$. These results coincide with the dynamical considerations on the mean-free-path λ (11).

On the basis of the above assumptions the following scaling form of the structure function is obtained:

$$S(\boldsymbol{q},\,t)=\phi(1-\phi)\bar{R}(t)^3\mathcal{S}(\bar{R}(t)q). \tag{19}$$

The scaled form $\mathcal{S}(Q)$ is given by

$$\mathcal{S}(Q)=\frac{4\pi}{3(1-\phi)}\Big\{\int_\rho \rho^3\Psi(\rho Q)^2 - \phi\int_\rho\int_{\rho'}(\rho+\rho')^3\Psi(\rho Q)\Psi(\rho' Q) \times \mathcal{G}((\rho+\rho')Q;\,K)\Big\}, \tag{20}$$

where

$$\int_\rho\cdots=\int\cdots\rho^3\Phi(\rho^3)3\rho^2 d\rho \tag{21}$$

and

$$\mathcal{G}(Q)=\Psi(Q)+\frac{3(K\sin Q/Q+\cos Q)}{Q^2+K^2}\,. \tag{22}$$

Let us discuss the limits $Q\ll 1$ and $Q\gg 1$: Expanding Eq. (20) the small Q part is given by

$$\mathcal{S}(Q)\cong\begin{cases}2.60\phi^{-1}Q^2 & \text{for } \phi\ll\phi_c\,,\\ 6.18Q^2 & \text{for } \phi\sim\phi_c\,.\end{cases} \tag{23}$$

The characteristic wavenumber has strong dependence of $\phi^{1/2}$ for $\phi\ll\phi_c$. On the other hand the large Q part is dominated by the single-droplet-part of Eq.(20) and has not such a strong depend-

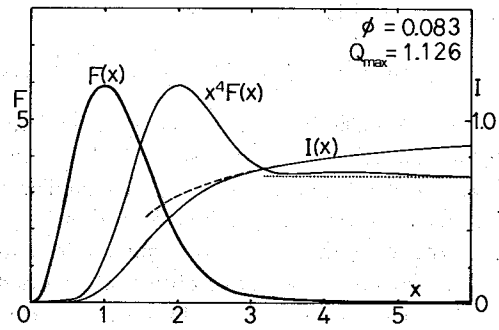

Fig. 1. Rescaled structure function $F(x)$ for $\phi=0.083$. $x^4F(x)$ and $I(x)$ are also shown. Broken line denotes the approximation (27). The scale for $x^4F(x)$ is not shown except for $x\to\infty$ limit (dotted line).

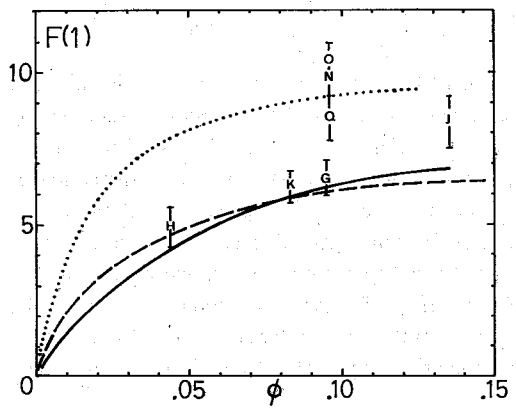

Fig. 2. Peak height $F(1)$. Present theory (solid line), Ohta's (broken line) and Rikvold and Gunton's (dotted line) are compared with experimental data by Knobler and Wong.

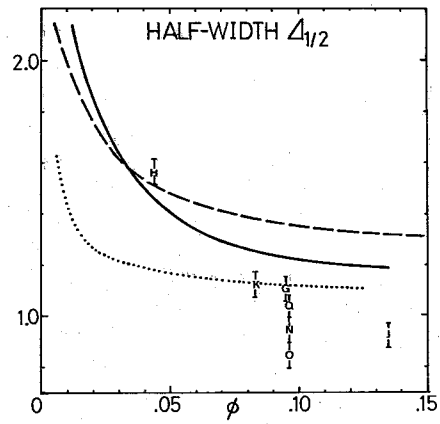

Fig. 3. Half-width $\Delta_{1/2}$ of $F(x)$. Details are the same as in Fig. 2.

ence. The tail is estimated as

$$\mathscr{S}(Q)\cong 6\pi\langle\rho^2\rangle/(1-\phi)Q^4\,, \tag{24}$$

where $\langle\rho^2\rangle=0.9027\cdots$ can be related to the interface area density $\mathcal{A}$, i.e., this is just the Porod law $S(q)=2\pi\mathcal{A}/q^4$. Note that in the mono-dispersive case[7] an oscillatory tail $\cos^2 Q/Q^4$ is found. Thus the characteristic wavenumbers in both regions $Q\ll 1$ and $Q\gg 1$ have different ϕ dependences, though they are scaled by the same $\bar{R}(t)$. The peak wavenumber $Q_{\max}$ is located between these two regions. In this sense $Q_{\max}$ is inadequate for a characteristic wavenumber.

In Fig. 1 the structure function for $\phi=0.083$ is shown after rescaling by $Q_{\max}$. The new scaling function $F(x)$ is introduced by

$$\mathscr{S}(Q)=Q_{\max}{}^{-3}F(Q/Q_{\max}). \tag{25}$$

The peak height $F(1)$ and the half-width $\Delta_{1/2}$ are compared with other theories and experiment by Wong and Knobler.[8] (Figs. 2~3.) Furukawa's scaling function[9] has not the ϕ dependence and is not referred here. The present results are in good agreement with Ohta's. In the comparison of $F(1)$ the experimental data are re-normalized because of the following reasons: In Ref. 8) the experimental data are normalized by the integrated intensity from $x=0.3$ to $x=3.0$. As is shown in Fig. 1 the integrated intensity $I(x)$ defined by

$$I(x)=\frac{}{(2\pi)^3}\int_0^x F(y)4\pi y^2 dy\,, \tag{26}$$

is rather slowly varing and $I(3.0)=65\sim 72\,\%$ for $\phi=0.04\sim\phi_c$ is found. This long tail is caused by the Q^{-4}-tail of $\mathscr{S}(Q)$ and is well approximated by

$$I(x)\cong 1-3\langle\rho^2\rangle/\pi(1-\phi)Q_{\max}x\,. \tag{27}$$

As a conclusion it should be remarked that though the Q^{-4}-tail is found in very far from peak position $x\gtrsim 3.0$ as is seen in Fig. 1, it affects the sum-rule considerably and one should be careful to normalize the scaling function.

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