Growth Rate of Critical Nuclei Near the Critical Point of a Fluid

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The growth rate of critical nuclei for a fluid near its critical point is discussed on the basis of the stochastic equation for the probability distribution function of the local order parameter, which was derived previously by the author. The growth rate was found to depend on ξ, the range of correlation of the order parameter fluctuation, and R, the radius of critical nuclei, as $\xi^0 R^{-3}$, in conformity with dynamical scaling. The rate of nucleation at the liquid–gas transition near the critical point is also discussed on the basis of this result.

1. INTRODUCTION

Recently there has been an increasing amount of attention being paid to phenomena occurring far from thermodynamic equilibrium.[2] Nucleation phenomena[2] and spinodal decomposition[3] are typical examples. These phenomena occurring in fluids in the vicinity of critical points have certain attractive features: Since the length scales involved are at least of the order of the range of correlations of critical fluctuations ξ, and the time scales involved are of the order of $\xi^3 f(\xi/R)$, where R is another length scale such as the radius of a critical nucleus,[4] a semimacroscopic treatment is quite

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[2] See, e.g., a number of the papers in Ref. 1.

effective. Indeed, such a treatment of the nucleation rate was recently presented by Langer and Turski[5] (LT) for the case of small supersaturation such that $R \gg \xi$ where, however, the growth rate of critical nuclei did not obey the dynamic scaling form[4] $\xi^{-3}\hat{f}(\xi/R)$.

On the other hand, we initiated another approach[6] to this sort of problem in deriving a stochastic equation obeyed by the probability distribution function of the local order parameter by eliminating in the first place all other rapidly varying variables near the critical point, in particular, the local transverse velocity, thus ensuring dynamic scaling from the outset. Since the growth rate of critical nuclei enters the prefactor in the expression for the nucleation rate,[5] here we present a calculation of the growth rate of critical nuclei on the basis of this stochastic equation.

In the next section we derive the macroscopic equation of motion for the average local order parameter on the basis of our stochastic dynamic equations.[6] In the subsequent section this macroscopic equation is linearized around an unstable steady-state solution with one critical nucleus. The linearized equation is then solved employing the method used by LT and the growth rate of critical nuclei is obtained as Eq. (31) below. Section 4 is devoted to the discussion of the nucleation rate on the basis of (31).

2. MACROSCOPIC EQUATION OF MOTION

Since there is a close parallel between the liquid–gas transition and critical mixing,[7] we treat both cases simultaneously by denoting the local order parameter by $a(\mathbf{r})$, meaning the local specific entropy and the local concentration in the respective cases. The stochastic dynamic equation for the probability distribution function $g(\{a\}, t)$ derived previously reads[3]

$$(\partial/\partial t)g(\{a\}, t) = H(\{a\})g(\{a\}, t) \tag{1}$$

with

$$
H(\{a\}) \equiv -L^0 \int d\mathbf{r} \, \frac{\delta}{\delta a(\mathbf{r})} \, \nabla^2 \left[k_B T \frac{\delta}{\delta a(\mathbf{r})} + \frac{\delta \Phi(\{a\})}{\delta a(\mathbf{r})} \right]
$$

$$
- \iint d\mathbf{r} \, d\mathbf{r}' \sum_{\alpha\beta} \frac{\delta}{\delta a(\mathbf{r})} \frac{\partial}{\partial r_\alpha} a(\mathbf{r})a(\mathbf{r}')\mathscr{T}^{\alpha\beta}(\mathbf{r} - \mathbf{r}')
$$

$$
\times \frac{\partial}{\partial r_\beta'} \left[k_B T \frac{\delta}{\delta a(\mathbf{r}')} + \frac{\delta \Phi(\{a\})}{\delta a(\mathbf{r}')} \right] \tag{2}
$$

where $\mathscr{T}^{\alpha\beta}(\mathbf{r})$ is the Oseen tensor given by

$$
\mathscr{T}^{\alpha\beta}(\mathbf{r}) \equiv \frac{1}{4\pi\eta} \left(\frac{1}{r} \delta_{\alpha\beta} + \frac{r_\alpha r_\beta}{r^3} \right) \tag{3}
$$

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[3] This equation is recast here in a more symmetric form using

$$
\sum_{\alpha} (\partial/\partial r_\alpha)\mathscr{T}^{\alpha\beta}(\mathbf{r}) = 0 \tag{1'}
$$

and η is the shear viscosity, which we assume to be constant in this work. $\Phi(\{a\})$ is the free energy associated with the fluctuation $\{a\}$ and is related to the equilibrium probability distribution $g_e(\{a\})$ through

$$g_e(\{a\}) = \text{const} \times \exp\left[-\Phi(\{a\})/k_B T\right] \tag{4}$$

Because of the enormous complexity of Eq. (1) with (2), we do not attempt to solve it but will be content with an approximation in which $g(\{a\}, t)$ on the right-hand side of (1) is replaced by the local equilibrium distribution function $g_l(\{a\}, t)$. This approximation is valid whenever one is in the "collision-dominated" regime and is the zeroth order approximation of the Chapman–Enskog expansion of gas dynamics.[8] The method of constructing the local equilibrium distribution function has already been variously discussed (see e.g., Ref. 9); one applies a field conjugate to the gross variables $\{a\}$ in the equilibrium state so as to bring the average values of $\{a\}$ to their true off-equilibrium values $\{\bar{a}\}$.

In the Gaussian approximation we then have

$$g_l(\{a\}) = \mathcal{N} \exp\left[-\sum \frac{1}{2\chi_{li}} (a_i - \bar{a}_i)^2\right]$$

$$= \mathcal{N} \exp\left\{-\frac{1}{2k_B T} \sum_i \frac{\partial^2 \Phi(\{\bar{a}\})}{\partial \bar{a}_i^2} (a_i - \bar{a}_i)^2\right\} \tag{5}$$

where we have expanded $a(\mathbf{r})$ in terms of a suitable orthogonal set of functions $\psi_i(\mathbf{r})$ as

$$a(\mathbf{r}) = \sum_i a_i \psi_i(\mathbf{r}) \tag{6}$$

so that

$$\langle (a_i - \bar{a}_i)(a_j - \bar{a}_j) \rangle_l = \chi_{li} \delta_{ij} \tag{7}$$

and the subscript l stands for the local equilibrium. However, there is a difficulty in this procedure in the present problem. The local equilibrium state with a critical nucleus cannot be constructed in this manner since χ_{li} with $i = 0$ describing the average square of fluctuations of the nucleation coordinate a_0 blows up and $\partial^2 \Phi(\{\bar{a}\})/\partial \bar{a}_0^2$ becomes negative. Hence we must suppress entirely the fluctuation of a_0 in the local equilibrium state. Choosing the radius of the nucleus as a_0 and denoting its value by R, we replace (5) by

$$g_l(\{a\}) = \mathcal{N} \exp\left\{-\frac{1}{2k_B T} \sum_i{}' \frac{\partial^2 \Phi(\{\bar{a}\})}{\partial \bar{a}_i^2} (a_i - \bar{a}_i)^2\right\} \delta(a_0 - R) \tag{8}$$

where the summation $\sum_i{}'$ excludes $i = 0$.

The right-hand side of (1) contains a factor

$$\left[k_B T \frac{\partial}{\partial a_i} + \frac{\partial \Phi(\{a\})}{\partial a_i}\right] g_l(\{a\}) \tag{9}$$

If we expand $\Phi(\{a\})$ around $\{a\} = \{\bar{a}\}$ and terminate at the quadratic terms, we immediately have for (9) with $i \neq 0$,

$$[\partial\Phi(\{\bar{a}\})/\partial\bar{a}_i]g_i(\{a\}) \tag{10}$$

Now, the first term of (9) contributes to fluctuations of a_i in the stochastic equation (1) and hence it is inconsistent to retain it for $i = 0$ since we have ignored fluctuation of a_0 entirely. Thus if we ignore the first term of (9) for $i = 0$, we see that (9) can be replaced by (10) for all i. In other words, we are allowed to make the following replacement in (1):

$$\left[k_B T \frac{\delta}{\delta a(\mathbf{r})} + \frac{\delta\Phi(\{a\})}{\delta a(\mathbf{r})} \right] g_i(\{a\}) \to \frac{\delta\Phi(\{\bar{a}\})}{\delta \bar{a}(\mathbf{r})} g_i(\{a\}) \tag{11}$$

With this preparation, we immediately find the macroscopic equation describing the time evolution of $\bar{a}(\mathbf{r})$ by multiplying both sides of (1) by $a(\mathbf{r})$ and by performing a functional integration over $\{a\}$ as follows:

$$\frac{\partial}{\partial t} \bar{a}(\mathbf{r}) = L^0 \nabla^2 \frac{\delta\Phi(\{\bar{a}\})}{\delta\bar{a}(\mathbf{r})} - \sum_{\alpha\beta} \int d\mathbf{r}' \, \mathcal{T}^{\alpha\beta}(\mathbf{r} - \mathbf{r}')$$

$$\times \left[\frac{\partial\bar{a}(\mathbf{r})}{\partial r_\alpha} \frac{\partial\bar{a}(\mathbf{r}')}{\partial r_\beta'} + \frac{\partial^2\chi_i(\mathbf{r}, \mathbf{r}')}{\partial r_\alpha \partial r_\beta'} \right] \frac{\delta\Phi(\{\bar{a}\})}{\delta\bar{a}(\mathbf{r}')} \tag{12}$$

where we have suppressed the argument t in $\bar{a}(\mathbf{r}, t)$ and

$$\chi_i(\mathbf{r}, \mathbf{r}') \equiv {\sum_i}' \chi_{li}\psi_i(\mathbf{r})\psi_i(\mathbf{r}') \tag{13}$$

is the correlation of fluctuations $\langle[a(\mathbf{r}) - \bar{a}(\mathbf{r})][a(\mathbf{r}') - \bar{a}(\mathbf{r}')]\rangle_l$ in the local equilibrium state, where the fluctuation of the nucleation coordinate is suppressed.

In this work we adopt the square gradient form for $\Phi(\{a\})$,[5]

$$\Phi(\{a\}) = \int [\tfrac{1}{2}K(\nabla a)^2 + \phi(a) - \mu a] \tag{14}$$

where μ plays the role of a chemical potential and K has only a weak critical anomaly like ξ^η.[4] Then (12) reduces to

$$\frac{\partial}{\partial t} \bar{a}(\mathbf{r}) = L^0 \nabla^2[-K \nabla^2\bar{a}(\mathbf{r}) + \phi'(\bar{a}(\mathbf{r}))]$$

$$- \sum_{\alpha\beta} \int d\mathbf{r}' \, \mathcal{T}^{\alpha\beta}(\mathbf{r} - \mathbf{r}')\left\{ \frac{\partial\bar{a}(\mathbf{r})}{\partial r_\alpha} \frac{\partial\bar{a}(\mathbf{r}')}{\partial r_\beta'} + \frac{\partial^2\chi_i(\mathbf{r}, \mathbf{r}')}{\partial r_\alpha \partial r_\beta'} \right.$$

$$\times \left. [-K \nabla'^2\bar{a}(\mathbf{r}') + \phi'(\bar{a}(\mathbf{r}'))] \right\} \tag{15}$$

where the prime on ϕ denotes differentiation with respect to its argument.

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[4] This η should not be confused with the shear viscosity η in (3). This dependence of K on ξ was chosen so as to yield a correct scaling form for $\langle\delta a'(\mathbf{r}) \delta a'(\mathbf{r}')\rangle$, where $\delta a'(\mathbf{r}) \equiv a(\mathbf{r}) - \bar{a}$.

3. GROWTH RATE OF CRITICAL NUCLEI

In order to obtain the growth rate of critical nuclei κ, we first linearize (15) with respect to the deviation $\delta a(\mathbf{r})$ of $\bar{a}(\mathbf{r})$ from its value $a^*(\mathbf{r})$ corresponding to a critical nucleus. Since $\Phi(\{a\})$ is extremum at $\{a\} = \{a^*\}$, we find

$$\kappa \, \delta a(\mathbf{r}) = L^0 \, \nabla^2[-K \, \nabla^2 + \phi''(a^*(\mathbf{r}))] \, \delta a(\mathbf{r})$$

$$- \sum_{\alpha\beta} \int d\mathbf{r}' \, \mathcal{T}^{\alpha\beta}(\mathbf{r} - \mathbf{r}') \left[\frac{\partial a^*(\mathbf{r})}{\partial r_\alpha} \frac{\partial a^*(\mathbf{r}')}{\partial r_\beta'} + \frac{\partial^2 \chi_i(\mathbf{r}, \mathbf{r}')}{\partial r_\alpha \, \partial r_\beta'} \right.$$

$$\left. \times \, [-K \, \nabla'^2 + \phi''(a^*(\mathbf{r}'))] \, \delta a(\mathbf{r}') \right] \tag{16}$$

where $\partial[\delta a(\mathbf{r})]/\partial t$ has been replaced by $\kappa \, \delta a(\mathbf{r})$ on the left-hand side.

If we envisage the same situation as was considered by LT,[5] namely a single critical nucleus with $R \gg \xi$ and a surface thickness of the droplet of the order of ξ, the method employed by LT to solve their hydrodynamic equation can be adopted here with slight modifications. First consider the region far from the droplet surface where $a^*(\mathbf{r})$ is constant. Here (16) is nothing but the equation describing the decay of fluctuations occurring in thermal equilibrium and we should have

$$\kappa \, \delta a(\mathbf{r}) = \nabla^2 \int d\mathbf{r}' \, \mathcal{L}(\mathbf{r} - \mathbf{r}')[-K \, \nabla'^2 + \phi''(a^*)] \, \delta a(\mathbf{r}') \tag{17}$$

where

$$\mathcal{L}(\mathbf{r}) = L^0 \, \delta(\mathbf{r}) + (\nabla^2)^{-1} \sum_{\alpha\beta} \frac{\partial^2}{\partial r_\alpha \, \partial r_\beta} \mathcal{T}^{\alpha\beta}(\mathbf{r})\chi(\mathbf{r}) \tag{18}$$

and

$$L = \int \mathcal{L}(\mathbf{r}) \, d\mathbf{r} \tag{19}$$

is nothing but the renormalized Onsager kinetic coefficient[10] [thermal conductivity or concentration conductivity apart from some unimportant coefficients; see (36) below]. The solutions in this region when the critical nucleus is centered at $\mathbf{r} = 0$ take the form

$$\delta a(\mathbf{r}) = (A/r) \sinh(qr) \qquad \text{inside droplet} \tag{20a}$$

$$\delta a(\mathbf{r}) = (B/r)e^{-q(r-R)} \qquad \text{outside droplet} \tag{20b}$$

Since we expect $q\xi \ll 1$ and $\mathcal{L}(\mathbf{r})$ is nonvanishing only for $|\mathbf{r}| \lesssim \xi$, we have

$$\kappa = LKq^2[-q^2 + \xi^{-2}] \tag{21}$$

where we have used the relation valid outside the interface[5]

$$\phi''(a^*) = K\xi^{-2} \tag{22}$$

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[5] We ignore the difference in $\phi''(a^*)$ inside and outside of the droplet.

then (21) yields

$$q \simeq (\kappa/LK)^{1/2}\xi \qquad (23)$$

provided that

$$(\kappa/LK)^{1/2}\xi^2 \ll 1 \qquad (24)$$

In the interfacial region we ignore the left-hand side of (16) since κ is small. We then find that by virtue of the property (1') the solution of (16) takes the form

$$\delta a(\mathbf{r}) = (C/r)\int dr'\, G(r, r') \qquad (25)$$

where $G(r, r')$ is the Green's function of radial coordinates, which satisfies

$$[-K(d^2/dr^2) + \phi''(a^*)]G(r, r') = \delta(r - r') \qquad (26)$$

Matching the solution (25) to the solutions (20a) and (20b) yields[6]

$$A \sinh(qR) = C/\phi''(a_1) \qquad (27a)$$

$$B = C/\phi''(a_2) \qquad (27b)$$

where a_1 and a_2 are the constant values of the order parameter taken far inside and far outside the droplet. We approximate $\phi''(a_1) \simeq \phi''(a_2) = K\xi^{-2}$. By making use of the spectral decomposition of $G(r, r')$ where only one term with negative eigenvalue is important for $r \simeq R$, we find near the interface

$$\delta a(\mathbf{r}) \simeq \frac{CR^2\, \Delta a}{2\sigma r}\frac{da^*(r)}{dr} \qquad (28)$$

where $\Delta a \equiv a_1 - a_2$ and σ is the "surface tension" given by

$$\sigma \equiv K\int_0^\infty [da^*(r)/dr]^2\, dr \qquad (29)$$

Having expressed $\delta a(\mathbf{r})$ in terms of κ and other supposedly known quantities, the final step in determining κ is to impose the conservation law condition

$$\int \delta a(\mathbf{r})\, d\mathbf{r} = 0 \qquad (30)$$

implied by (16). Thus, in the approximation $\xi \ll R$, we finally obtain

$$\kappa = 2\sigma L/(\Delta a)^2 R^3 \qquad (31)$$

provided that $qR \ll 1$.

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[6] Since we closely follow LT up to (31) except for the relationship between κ and q, we present here only a brief outline of the derivation.

The critical behavior of the growth rate κ can be found by noting the critical behavior of various quantities entering (31):

$$\sigma \sim \xi^{1-(2-\alpha')/\nu'} \qquad \text{(Ref. 11)} \tag{32a}$$

$$L \sim \xi^{\gamma'/\nu'-1} \qquad \text{(Refs. 4, 7, and 10)} \tag{32b}$$

$$\Delta a \sim \xi^{-\beta/\nu'} \qquad \text{(Ref. 12)} \tag{32c}$$

where the critical exponents refer to those in the ordered phase. With the use of the scaling law relation $\alpha' + 2\beta + \gamma' = 2$ we find

$$\kappa \sim \xi^0 R^{-3} \tag{33}$$

which is of the dynamical scaling form, as mentioned in Section 1.[4,7,10] Using $K \sim \xi^\eta$ and the relation $\gamma' = (2 - \eta)\nu'$, the consistency condition of (31) is also verified: $qR \sim (\xi/R)^{3/2} \ll 1$. Relations (31) and (33) are the main results of this work. Since we have eliminated other degrees of freedom than the order parameter at the outset, there is no need to consider the thermal nonaccommodation effects, again in contrast to the Langer–Turski approach.

Let us now compare (31) and (33) with the results of LT. Langer and Turski[5] obtained the following results for the growth rate of a critical nucleus for the liquid–gas transition: (i) When the thermal nonaccommodation effects are unimportant,

$$\kappa = [2\sigma n_v/mR^3(\Delta n)^2]^{1/2} \sim \xi^{-(1-\eta)/2}R^{-3/2} \tag{34}$$

(ii) When the thermal nonaccommodation effects are very important,

$$\kappa = 2\lambda\sigma T/l^2 R^3(\Delta n)^2 \sim \xi^{1+\eta}R^{-3} \tag{35}$$

where $\Delta n = n_l - n_v$, and n_l and n_v are the number density of molecules in the vapor and liquid phases, respectively, and λ and l are the thermal conductivity and the latent heat per molecule, respectively. Here, in addition to (32) we have used $\lambda \sim L$, $\Delta n \sim \Delta a$, $l \sim \Delta a$, and the scaling law relations among critical exponents.[12]

We note that the both growth rates (34) and (35) are much greater than ours near the critical point because in the Langer–Turski approach the rapidly varying transverse local velocity plays an important role, which has been eliminated at the outset in our approach.

It is interesting to note that the growth rate (31) is the same as that which would result from the stochastic equation (1) with (2) if the second term of (2) is dropped and L^0 in the first term is replaced by L. This is due to a certain insensitivity of the specific method by LT to solve (16) to the details of the equation.

4. RATE OF NUCLEATION

It is natural to study the nucleation rate near the critical point on the basis of the growth rate of critical nuclei we have obtained in the preceding

section. There are, however, a few problems to be solved before we can do this satisfactorily. First, since our starting equation (2) has a rather complicated form in which the "diffusion constant" also depends quadratically on {a}, Langer's formal theory of nucleation[13] cannot be used immediately. Second, near the critical point, where the length scales involved tend to infinity, the interaction among critical droplets can become important. Nevertheless, pending the resolution of these problems, it would still be of some interest to discuss the nucleation rate at the liquid–gas transition by naively replacing the growth rate of critical nuclei of Langer and Turski by ours.[7]

For this purpose let us rewrite (31) for the case of the liquid–gas transition where $a(\mathbf{r})$ is $n(\mathbf{r})$, which for the most part exhibits a diffusive behavior near the critical point with L given by

$$L = (n^2 \chi_T / \rho C_p) \lambda \tag{36}$$

Here χ_T is the isothermal compressibility. Substituting (36) into (31) and using (35), we obtain the following for the ratio of the growth rates obtained here and by LT[8]:

$$\frac{(\kappa)_{\mathrm{K}}}{(\kappa)_{\mathrm{LT}}} = \left(\frac{ln}{T}\right)^2 \left(\frac{\partial T}{\partial p}\right)_s \left(\frac{\partial T}{\partial p}\right)_V \simeq \left[\frac{l_0 n}{T} \left(\frac{\partial T}{\partial p}\right)_V\right]^2 \epsilon^{2\beta} \tag{37}$$

where $\epsilon \equiv (T_c - T)/T_c$ and we have used with finite l_0

$$l \approx l_0 \epsilon^{\beta} \tag{38}$$

The critical supercooling for a saturated vapor, δT_c, corresponding to the nucleation rate I_c, now becomes

$$\delta T_c = \tau_0 \epsilon [\ln(V J_0 / I_c) + \phi \ln \epsilon - \ln(\delta T_c / T_c)]^{-1/2} \tag{39}$$

where V is the entire volume of the system. This equation is of the same form as that given by LT, where the explicit form of the finite constant τ_0 is given by (7.14) of LT. However, the finite constants J_0 and ϕ are different:

$$J_0 = (J_0)_{\mathrm{LT}} \left[\frac{l_0 n}{T} \left(\frac{\partial T}{\partial p}\right)_V\right]^2 \tag{40}$$

$$\phi = (\phi)_{\mathrm{LT}} + 2\beta \tag{41}$$

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[7] Note that the extra degrees of freedom associated with the velocity field in the Langer–Turski theory have no effect on the statistical prefactor and the activation free energy as shown by them.

[8] Equation (36) follows from the relations $L\phi'' = \lambda/\rho C_p$ and $\phi'' = 1/n^2\chi_T$. In obtaining (37), we have used $\chi_T/\rho C_p = T^{-1}(\partial T/\partial p)_s(\partial T/\partial p)_V$ and also $(\partial T/\partial p)_s \simeq (\partial T/\partial p)_V$ near the critical point.

where $(J_0)_{\text{LT}}$ and $(\phi)_{\text{LT}}$ are the values of J_0 and ϕ given by the LT equations (7.22) and (7.21), respectively. In particular, using the values of critical exponents listed by LT, we have

$$\phi = 9\nu' - 2\beta - \gamma' + 1 \approx 4.25 \qquad (42)$$

In view of the problems mentioned at the beginning of this section, we refrain from any further discussion of the nucleation rate at this time.

5. CONCLUDING REMARKS

In the preceding sections we exemplified the usefulness of the dynamical equations (1) and (2) for the order parameter by calculating the growth rate of critical nuclei near the critical point of fluid. This sort of equation naturally extends the mode coupling ideas of critical dynamics[4,7,10,14] to far-from-equilibrium situations. Note, in particular, that near a critical point even a very small deviation from thermal equilibrium appears greatly magnified and hence the usual linear approximation quite often breaks down. We hope to report on these problems, including spinodal decomposition of a fluid near a critical point,[3] in the near future.

ADDENDUM

After this paper was submitted for publication, Professor J. S. Langer communicated to the author an error in the calculation of the thermal nonaccommodation effect of LT, and he now obtains the growth rate which is quite similar to our Eq. (31).

Recently we were able to reduce Eqs. (1) and (2) to a simpler stochastic equation for the probability distribution function of the nucleation coordinate using a local equilibrium approximation. This simpler equation is susceptible to analysis by the method of Langer[13] where the growth rate (31) now enters in a natural way.

ACKNOWLEDGMENTS

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