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Communication: On the diffusion tensor in macroscopic theory of cavitation

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The classical description of nucleation of cavities in a stretched fluid relies on a one-dimensional Fokker-Planck equation (FPE) in the space of their sizes r, with the diffusion coefficient $D(r)$ constructed for all r from macroscopic hydrodynamics and thermodynamics, as shown by Zeldovich. When additional variables (e.g., vapor pressure) are required to describe the state of a bubble, a similar approach to construct a diffusion tensor $\hat{D}$ generally works only in the direct vicinity of the thermodynamic saddle point corresponding to the critical nucleus. It is shown, nevertheless, that "proper" kinetic variables to describe a cavity can be selected, allowing to introduce $\hat{D}$ in the entire domain of parameters. In this way, for the first time, complete FPE's are constructed for viscous volatile and inertial fluids. In the former case, the FPE with symmetric $\hat{D}$ is solved numerically. Alternatively, in the case of an inertial fluid, an equivalent Langevin equation is considered; results are compared with analytics. The suggested approach is quite general and can be applied beyond the cavitation problem. *Published by AIP Publishing.* [http://dx.doi.org/10.1063/1.4997934]

Cavitation is of enormous interest in many technological and scientific applications, ranging from the explanation of erosion of turbine blades to particle detection in bubble chambers.[1,2] The recent experimental[1,3] and molecular dynamics studies[4] further challenge the theoretical understanding of various cavitation mechanisms. In addition, the theory of cavitation can provide a broader insight into the plethora of other nucleation phenomena.[5] In particular, Zeldovich's description[6] of formation of a cavity in a stretched viscous fluid crowned what is now known as the "classical theory of nucleation" by providing the first example of a *macroscopic* derivation of the diffusion coefficient $D(R)$ responsible for the random walk of a nucleus in the space of its sizes.

Generalization of the macroscopic approach for the case of multiparametric nucleation (when extra variables, such as fluctuating pressure, are required to characterize a nucleus) is straightforward only in the vicinity of the saddle point,[7–9] the multidimensional equivalent of the critical size. While the saddle point properties are sufficient for some of the analytical conclusions (see below), the full description of the cavitation problem requires specification of the Fokker-Planck equation (FPE) for the entire domain of the parameters. Currently, in the absence of appropriate FPE's, there are practically no numerical simulations of the early (nucleation) stages of cavitation. This is in contrast to the problem of multicomponent condensation where the *microscopic* diffusion tensor is introduced and where a large amount of numerical work has been performed.[5,10] Analytical descriptions could also benefit from having a complete FPE since many nucleation issues require an off-saddle point analysis.[9] The intent of the present communication is thus to demonstrate a possibility of a macroscopic construction of a complete diffusion tensor, generalizing the 1-dimensional Zeldovich approach. Specifications will be made for the cavitation problems in volatile and inertial fluids. Numerical simulations will follow, with accuracy sufficient to extract the pre-exponential of the nucleation rate. Comparison of the results with available expressions will clarify connection between single- and multidimensional descriptions.

Let us start with the original problem[6] of formation of an empty cavity of radius R in a viscous fluid under negative pressure P. The critical radius $R_* = 2\sigma/(-P)$ with σ being the surface tension is determined by the balance between P and the Laplace pressure, and in what follows, the asterisk will indicate a function evaluated at R_*. The minimal work to form a cavity is given by $W(R) = W_* w_0(r)$, with $w_0(r) = 3r^2 - 2r^3$, $r = R/R_*$, and $W_* = 4\pi\sigma R_*^2/3$. If $R \neq R_*$, the cavity will grow/decay in accord with macroscopic hydrodynamic equations, $\dot{R} = (R - R_*)\,|P|/4\eta$, η being the viscosity. Further, a FPE for the distribution of cavities over sizes $f(R, t)$ is constructed as $\partial f/\partial t = -\partial j/\partial R$, where the flux along the R axis is given by $j = -Df^{eq}\,(\partial/\partial R) f/f^{eq}$ with $f^{eq}(R) \sim \exp(-W/T)$ being the quasiequilibrium distribution (the Boltzmann constant is taken as 1). The diffusion coefficient $D(R)$ has to ensure transition to correct drift flux $\dot{R}f$ in the case of a smooth distribution. This leads to the "Einstein relation" in the R-space[6] with

$$D(R) = -T\dot{R}\,/(dW/dR). \tag{1}$$

The nucleation rate I is then obtained from the asymptotic solution of a Fokker-Planck equation with the stationary flux given by[6]

$$I = \frac{\lambda_0}{\sqrt{2\pi}} f^{eq}(R_*)\left(-\frac{1}{T}\frac{d^2W}{dR^2}\bigg|_*\right)^{-1/2},\ \lambda_0 = \frac{d\dot{R}}{dR}\bigg|_*. \tag{2}$$

Subsequently, when evaluating λ_0 in the above equation, Kagan[11] discussed various kinetic effects due to inertia, evaporation, and heat conductivity of the fluid. Two- and multidimensional FPE's were later considered, e.g., in Refs. 7–9,

based on a generalized FPE for the distribution $f(\vec{u},t)$ with a d-component $\vec{u}=(r,z,\ldots)$ and $f^{eq}(\vec{u})\sim\exp[-W(\vec{u})/T]$,

$$\frac{\partial f}{\partial t}=-\hat{\nabla}\cdot\vec{j},\ \vec{j}=-f^{eq}\hat{D}\cdot\left(\hat{\nabla}\frac{f}{f^{eq}}\right). \tag{3}$$

Here z represents "additional variables" (to be specified below) that characterize the state of an r-sized nucleus and the diffusion tensor $\hat{D}$ is linked to the deterministic (macroscopic) rate $\dot{\vec{u}}$ via

$$\dot{\vec{u}}=-\frac{1}{T}\hat{D}(\vec{u})\cdot\hat{\nabla}W(\vec{u}). \tag{4}$$

The work $W(\vec{u})$ has a saddle point at $\vec{u}=\vec{u}_*$ and the stationary flux across the saddle had been derived in a non-cavitation context as[12]

$$I=\lambda_0 Q f^{eq}(r_*,z_*),\ Q=\frac{(2\pi)^{d/2-1}}{\sqrt{-\det\hat{V}}}. \tag{5}$$

The analog of λ_0 in Eq. (2) is defined as the positive eigenvalue of the kinetic (Jacobian) matrix $\hat{K}=\hat{\nabla}\dot{\vec{u}}$ and the Hessian matrix $\hat{V}=(1/T)\left(\hat{\nabla}\hat{\nabla}\right)W(\vec{u})|_*$ describes the shape of the saddle. The technique of simultaneous diagonalization of the symmetric tensors $\hat{D}_*$ and $\hat{V}$, which leads a straightforward derivation of the flux I, also allows the time-dependent treatment of the cavitation problem.[9] In the case of inertial effects with non-symmetric $\hat{D}$, such a diagonalization is impossible but the general equation (5) remains adequate, being equivalent to Kramers solution for a barrier crossing in the overdamped limit.[13]

In a general situation, the issue of reconstructing $\hat{D}$ at arbitrary $\vec{u}$ remains. The apparent similarity of the multidimensional equation (4) with Eq. (1) is deceptive. Indeed, a symmetric d-dimensional tensor has $d(d+1)/2$ independent components, while Eq. (4) gives only d relations between them—a situation which can be uniquely resolved only for $d=1$. On the other hand, if there exists a set of variables $\vec{u}$ such that $\hat{D}(\vec{u})$ is diagonal everywhere, one needs only d independent components, which allows us to generalize Eq. (1) as

$$\hat{D}(\vec{u})=-T\,\mathbf{diag}\left\{\dot{\vec{u}}\Big/\hat{\nabla}W\right\} \tag{6}$$

(the symbol **diag** indicates the diagonal matrix). The consistency of the treatment is indicated by positive non-singular values of the diagonal elements for the entire domain of $\vec{u}$. Similar ideas can be used for antisymmetric $\hat{D}$, as will be discussed below. When such a set of "proper" kinetic variables $\vec{u}$ can be found, as in the case of cavitation, the coefficients of the FPE can be deduced solely from macroscopic kinetics ($\dot{\vec{u}}$) and thermodynamics (W).

Volatile fluid. When selecting the additional variable to characterize the state of a bubble, one can choose between the vapor pressure P_v or the number of molecules n inside a bubble. The former leads to a diagonal $\hat{V}$,[9] the latter results in a diagonal $\hat{D}$ and is preferable in the present context. Specifically, $z=n/n_*$ will be used, where n_* is the number of molecules in a critical bubble. If the vapor is treated as an ideal gas, the work W is known[11] and in current variables is given by

$$\frac{1}{W_*}W(r,z)=w_0(r)+\frac{2}{b}\left(r^3-z\left(1-\ln\frac{z}{r^3}\right)\right). \tag{7}$$

Here $b=1-P/P_{v,*}$ (where $P_{v,*}$ is the equilibrium vapor pressure), $R_*=2\sigma/bP_{v,*}$, and $W_*/T=\frac{1}{2}bn_*$. In order to dimensionalize the growth rates, time will be measured in units of $4\eta/(bP_{v,*})$, where η is the viscosity, and the dimensionless evaporation rate will be defined as $\theta\simeq\sqrt{6/\pi}\alpha_c v_T\eta/\sigma$, with α_c as the condensation coefficient and v_T as the thermal velocity of vapor molecules. One has

$$\dot{r}=r-1+\frac{1}{b}\left(\frac{z}{r^2}-r\right),\ \dot{z}=\theta r^2\left(1-\frac{z}{r^3}\right). \tag{8}$$

The first equation corresponds to the viscous limit of the Rayleigh-Plesset equation, while $\dot{z}$ is determined by the difference of the evaporation and condensation rates on the surface of the bubble. The θ-independent conditions $\dot{r}(r,z)=0$ and $\dot{z}(r,z)=0$ correspond to mechanical and chemical equilibrium, respectively. The below two equations determine $\hat{K}_*$ and $\hat{V}$,

$$\hat{K}_*=\begin{pmatrix}1-3/b & 1/b\\ 3\theta & -\theta\end{pmatrix},\ \hat{V}=6\frac{W_*}{T}\begin{pmatrix}3/b-1 & -1/b\\ -1/b & 1/3b\end{pmatrix}. \tag{9}$$

Evaluation of the eigenvalue λ_0 from $\det\left|\hat{K}_*-\lambda\hat{\mathrm{I}}\right|=0$ (with $\hat{\mathrm{I}}$ being a 2×2 identity matrix) leads to an elementary quadratic equation, and following Ref. 9, only the leading terms as $\theta\to0$ are presented explicitly (note that $\hat{K}_*$ and thus λ_0 are invariant upon transformation of variables). For $\theta\ll|b-3|$,

$$\lambda_0\simeq\begin{cases}\dfrac{b\theta}{3-b}, & b<3,\\ 1-3/b, & b>3.\end{cases} \tag{10}$$

A zero limit for $\theta\to0$ and $b<3$ implies that for a vanishingly small evaporation rate, empty, rather than filled, cavities will be nucleated.[9] From λ_0 and $\sqrt{-\det\hat{V}}=n_*\sqrt{3b}$, one obtains the nucleation rate in Eq. (5).

From Eq. (9), one gets a diagonal $D_*=-\hat{K}_*\cdot\hat{V}^{-1}$. This strongly simplifies its evaluation at arbitrary (r,z). From Eq. (6), one has

$$\hat{D}(r,z)=\frac{T}{6W_*}\mathbf{diag}\left\{\frac{1}{r},\ 3b\theta\frac{z/r-r^2}{\ln(z/r^3)}\right\}. \tag{11}$$

Formally, adding a certain symmetric tensor $\delta\hat{D}(r,z)$ with a zero determinant and with zero components at (r_*,z_*) would lead to the same $\dot{r}$ and $\dot{z}$ in Eq. (4). Nevertheless, symmetry—in this case, the diagonal structure of $\hat{D}_*$—is a powerful property and at least from a macroscopic point, it is unlikely to abruptly break down in the non-saddle region.

Once $\hat{D}(r,z)$ was specified, the FPE, Eq. (3) was discretized on a 200×200 grid with spacing $\delta r=\delta z=0.01$ so that the upper boundaries $r_{\max}=z_{\max}=2$ are sufficiently far from the saddle located at $r_*=z_*=1$. A Dirichlet-type boundary condition $f(\delta r,z)=A\exp[-W_*w(\delta r,z)/T]$ was used at the smallest size, while a reflecting (Neumann-type) boundary with $j_z(r,0)=0$ was used for empty cavities. The value of the normalization constant A does not matter as long as the scaled rate $I/f^{eq}(r_*,z_*)$ is considered. Absorbing boundaries $f(r_{\max},z)=f(r,z_{\max})=0$ were assumed on the two other sides of the square. In the stationary limit, one obtains a set of linear equations for $f(r,z)$ at the grid points, which was solved using *Mathematica*. A more stable (also, more time-consuming) alternative is

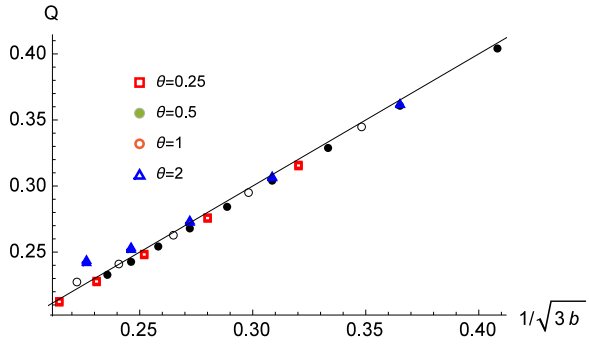

FIG. 1. Thermodynamic part of the nucleation pre-exponential $Q = I/[\lambda_0 f^{eq}(r_*, n_*)]$ for cavitation in a volatile fluid. Symbols—numerics (from the Fokker-Planck equation); line—$Q = 1/\sqrt{3b}$.

the propagation of the time-dependent solution. The rate I was calculated as the total flux across the right and the upper boundaries. The results were used to determine the pre-exponential of the nucleation rate, as in Fig. 1. After the unstable eigenvalue λ_0 is scaled out, almost all numerical data become insensitive to kinetics and collapse on the expected thermodynamic curve (which appears perfectly smooth at $b = 3$). Minor deviations at extreme θ are likely due to moderate values of the nucleation barrier $W_*/T = 25$ used in simulations.

Having confirmed the accuracy of the 2-dimensional treatment, we return to Eq. (2). One has for the 1-dimensional equilibrium distribution over sizes

$$f^{eq}(r) = \int_0^\infty dz f^{eq}(r,z) \simeq A\sqrt{\frac{2\pi r^3}{n_*}}\exp\left[-\frac{W_* w_0(r)}{T}\right]. \tag{12}$$

The major contribution to the integral comes from the vicinity of the line of chemical equilibrium $z = r^3$, and $w_0(r) = 3r^2 - 2r^3$ describes the reduced work to create a corresponding bubble. If the factor A is not assumed constant, it should be evaluated on the same line. After that Eq. (2) gives the same rate I; λ_0 can be determined either as $d\dot{r}/dr|_*$ along the growth/decay trajectory[11] (which is different from the chemical equilibrium for finite θ) or as a positive eigenvalue of $\hat{K}_*$. At the same time, there are subtleties associated with the "quasi-1-dimensional description" when the Zeldovich equation (2) is applied in the multiparametric situations. For example, if one re-writes it in terms of the number of molecules in a bubble rather than in terms of its radius, which implies swapping r and z in Eq. (2) and under the integral in Eq. (12), this integral diverges for $b \geq 3$ and $f^{eq}(n)$ is not defined. The latter is related to the breakdown of the original Döring's approach in this region.

Inertial fluid. Let us follow notations in Ref. 14 introducing a dimensionless "inertial size" $r_{in} = 8\eta^2/(\rho\sigma R_*)$ with ρ being the density of the fluid and using "time" t time measured in units of $4\eta/|P|$. In addition to "potential energy" $w_0(r) = 3r^2 - 2r^3$, the dimensionless work includes kinetic energy of the surrounding fluid;[8] in current variables,

$$\frac{1}{W_*}W(r,\dot{r}) = w_0(r) + \frac{1}{2}m(r)\dot{r}^2\,,\; m(r) = \frac{6r^3}{r_{in}}. \tag{13}$$

Here $m(r)$ is the "associated mass." The growth/decay rate of a cavity follows from the dissipation relation $\dot{w} = -6r\dot{r}^2$ and is given by the dimensionless version of the Rayleigh-Plesset equation with negligible vapor pressure inside the cavity,

$$\dot{r} = r - 1 - \frac{r}{r_{in}}\left(r\ddot{r} + \frac{3}{2}\dot{r}^2\right). \tag{14}$$

Nucleation can be described as a random walk in the $(r, \dot{r})$ space and, except for an r-dependent mass, is close to the Kramers escape problem.[13,15] In view of the current emphasis on the symmetry (antisymmetry) of the diffusion tensor, the "best" kinetic variable, however, is the associated generalized momentum $p = m(r)\dot{r}$, similar to the case of quantum cavitation.[16] Using $h(r, p) = w_0(r) + p^2/2m(r)$ as a "reduced Hamiltonian," one has an equivalent representation of Eq. (14),

$$\dot{r} = \frac{\partial h}{\partial p}\,,\; \dot{p} = -\frac{\partial h}{\partial r} - p\frac{r_{in}}{r^2}, \tag{15}$$

with the last term describing the "friction force."

The quasiequilibrium distribution is given by $f^{eq}(r,p) = A\exp\left[-W_* h(r,p)/T\right]$. Unlike the previous case of the volatile fluid where the pre-exponential could be specified within the classical theory only as "a slowly changing function," in the (r, p) space, a constant A is well justified since it complies with the Gibbs distribution. Thus, it makes sense to evaluate A explicitly. The 1-dimensional distribution $f^{eq}(r)$ is similar to the one in Eq. (12) with n_* replaced by $r_{in}W_*/6T$. Assuming a known number of primary bubbles and keeping in mind that the leading asymptotic approximation can be insufficient when not-too-large barriers are of interest (see below), one obtains an asymptotic series for normalization per bubble,

$$A = \left(\frac{W_*}{T}\right)^{\frac{7}{4}}\frac{3^{\frac{3}{4}}\sqrt{r_{in}}}{\sqrt{\pi}\,\Gamma\left(\frac{5}{4}\right)}\left(1 + \sum_n{}'\left(\frac{4T}{27W_*}\right)^{\frac{n}{2}}\frac{\Gamma\left(\frac{5}{4}+\frac{3n}{2}\right)}{n!\,\Gamma\left(\frac{5}{4}\right)}\right)^{-1}. \tag{16}$$

Here $\Gamma(x)$ is the Gamma function and the prime indicates that summation should be terminated once the smallest term is achieved.

To evaluate the nucleation rate, one can use the simplest equation (2). The positive eigenvalue of the kinetic matrix $K_* = \partial(\dot{r}, \dot{p})/\partial(r,p)|_*$ (with $r_* = 1$, $p_* = 0$) coincides with the Kramers expression[13] if the mass of the particle is fixed at the critical value $m(r_*) = 6/r_{in}$,

$$\lambda(r_{in}) = \frac{1}{2}\left(\sqrt{r_{in}^2 + 4r_{in}} - r_{in}\right) \tag{17}$$

(see also Refs. 8 and 17), with the viscous limit $r_{in} \to \infty$ corresponding to $\lambda \to 1$. Thus,

$$I = \lambda(r_{in})\tilde{I}\,,\; \tilde{I} = A\left(\frac{W_*}{T}\right)^{-1}\sqrt{\frac{m(r_*)}{6}}\,e^{-W_*/T}. \tag{18}$$

Similarly, the same result follows from Eq. (5) with $\hat{V} = (W_*/T)\,\mathbf{diag}\{-6, 1/m(r_*)\}$ and $Q = T/\left(W_*\sqrt{r_{in}}\right)$. Due to normalization, the pre-exponential $\tilde{A} = I\exp(W_*/T)$ differs from earlier expressions and will be verified numerically below. For small η and large $W_* \gg kT$, one has in dimensional units $\tilde{A} \simeq 4\pi^{1/4}\Gamma^{-1}\left(\frac{5}{4}\right)\sigma^{5/4}T^{-3/4}\rho^{-1/2}$. The latter is non-singular near the line of the phase equilibrium $W_* \to \infty$ and evaluates to about 10^{13} s^{-1} for a water-like

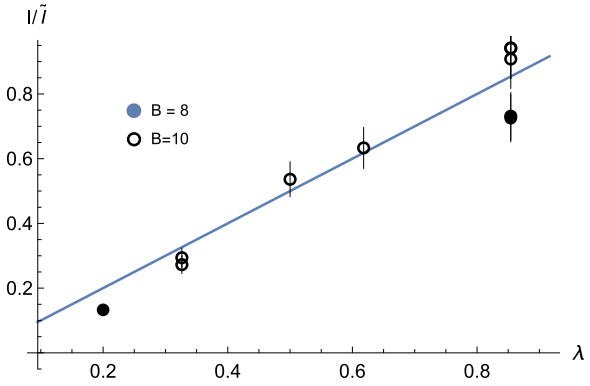

FIG. 2. Kinetic part of the pre-exponential in inertial cavitation for two values of the dimensionless barrier $B = W_*/T$. The values of λ, Eq. (17), can range between 0 and 1 corresponding to non-viscous and highly viscous limits, respectively. Symbols—simulations based on the Langevin equation; line—from Eq. (18).

fluid albeit with negligible viscosity. The analog of the underdamped Kramers solution mentioned in Ref. 6 is not required even for $\eta \to 0$[9] due to vanishing mass $m(r)$ as $r \to 0$, which always makes the problem "overdamped" at small sizes.

From here, we can proceed in evaluating $\hat{D}(r,p)$. To keep the antisymmetric structure of $\hat{D}_* = -\hat{K}_* \cdot \hat{V}^{-1}$, one constructs

$$\hat{D}(r,p) = \frac{T}{W_*}\begin{pmatrix} 0 & -1 \\ 1 & 6r \end{pmatrix}. \tag{19}$$

This specifies the FPE for cavitation limited by viscosity and inertia of the fluid. Again, we reject the possibility of adding a correcting tensor $\delta\hat{D}(r,z)$, even if Eq. (4) is satisfied, since that would violate the symmetry.[18]

In practice, the numerical solution of Eq. (3) with an asymmetric tensor $\hat{D}$ can be complicated. Instead, one can use a discrete version of the Langevin equation describing the stochastic evolution of a single cavity. (This is similar to simulations of the Kramers problem, e.g., Ref. 19, albeit with an r-dependent mass.) If one considers a small time increment δt and a random variable $\xi(t) = \pm 1$, the changes of the radius Δr and the momentum Δp of a cavity are given by

$$\Delta p = \dot{p}\delta t + \sqrt{2\delta t D_{pp}}\,\xi(t)\,,\ \Delta r = \frac{p}{m(r)}\delta t. \tag{20}$$

When solving the Langevin equation, the barrier (and thus the exponential part of the nucleation rate) is determined by the noise intensity. This makes extraction of the pre-exponential more challenging than in the case of the FPE for the volatile fluid described earlier, where the correct barrier is introduced from the start via the input of $f^{eq}(r,z)$. In addition, since the associated mass of the cavity vanishes as $r \to 0$, a rather small time step δt has to be selected, while a reflecting boundary is required at some small $r_{\min}$ to prevent the simulated particle from approaching the singularity. Thus, smaller barriers $W_*/T \sim 10$ were used, with $r_{\min} = 0.05$ and $\delta t \sim 0.000\,125 - 0.000\,062\,5$. Simulations were done with *Mathematica*, with about 100 runs for each data point; the rates I were determined as the inverse averages of the waiting time for the cavity to reach a size of $r = 2$ (using the inverses of the standard deviations[20] gave comparable values). Results for the kinetic part of the pre-exponential are shown in Fig. 2; doubling of some symbols is due to doubling of the time step for the same parameters and the indicated statistical scatter is about 10%.

In conclusion, the study describes a general macroscopic approach to constructing a diffusion tensor for the multiparametric nucleation problem, which generalizes the 1-dimensional Zeldovich method. This allows us to fully specify the multidimensional Fokker-Planck equation (FPE) in the entire space of the parameters of a nucleus, as shown explicitly for cavitation in viscous volatile and inertial fluids. The FPE, or its stochastic counterpart, the Langevin equation, can be solved with accuracy which is sufficient to extract the pre-exponential of the nucleation rate. This opens the possibilities of future descriptions of cavitation, as well as other nucleation problems, which are not restricted to the saddle point approximation and which would clarify the role of selected boundary conditions, time dependent effects, redistribution of nucleation paths, etc.

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