Shape Fluctuations of Spherical Micelles

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The thermal excitation of capillary waves on the surface of a spherical micelle has been analysed in an approximate manner using a series expansion in spherical harmonics and restricting the treatment to small amplitudes. The potential energy governing the dynamics of these motions is computed as the surface tension, γ, of the micelle multiplied by its surface area, A. It is found that a closed, ordinary surfactant micelle in aqueous solution with $\gamma \approx 25$ mN m^{-1} exhibits a root-mean-square dispersion, σ_r/R, of its radius of several percent because of shape fluctuations on the time-scale 10^{-10} s. The present study also indicates that (closed) micellar or microemulsion droplets with $\gamma \lesssim 1$ mN m^{-1} experience large fluctuations in geometry.

Ordinary surfactant micelles in aqueous solution are generally considered as small hydrocarbon droplets of variable size, with ionic groups at the hydrocarbon/water interface.[1] Deviations caused by the thermal motion from a strictly spherical geometry are usually assumed to be of minor importance.[2,3] The excess free energy of this kind of micelle can be characterized (at least partially) by means of its (mechanical) surface tension γ, the value of which normally falls in the range 5–30 mN m^{-1} according to recent estimates.[4,5] The considerable pressure-raising effect of this micelle surface tension appears to be a major factor determining the solubilization of lipophilic substances and gases in micellar solutions.[6]

In this paper we follow a theoretical line that goes back to the treatment of capillary waves on a liquid droplet in air of Lord Rayleigh.[7] Hence we shall assume that the mechanical behaviour of even a very small (oil-in-water or water-in-oil) spherical micelle with radius R in the interval $2.0 \leqslant R/\text{nm} \leqslant 10.0$ can be modelled in a satisfactory way by means of a tension that is attributed to a dividing surface located at the hydrocarbon/water interface.† A change in shape resulting in an increase of the micelle surface area, A, will thus cause a free-energy increase that can be estimated as $\gamma \Delta A$, insofar as $\Delta A/A$ is small. Our approach implies that such free-energy terms which are associated with displacements of the surface of tension along the direction of its normal (disjoining pressure terms) are supposed to add up to approximately zero for a closed micelle with fixed volume. This *ansatz* should provide a reasonable first approximation, particularly as our treatment is restricted to surface vibrations of small amplitude.

We may then anticipate that when the inequality $\gamma A \gg kT$ is fulfilled, large distortions of the spherical geometry will effectively not occur. The questions scrutinized in this work concern the consequences of the transition from a fairly high to a comparatively low value of γ for spherical, liquid aggregates of micellar size on the average fuzziness of the boundary between the micelle core and the exterior continuous phase. As will be seen, the capillary wave motions for a micelle have frequencies of the order of 10^{10} Hz. For comparison, we note that the lifetime

† This non-trivial assumption is elucidated in a forthcoming paper by J. C. Eriksson, S. Ljunggren and U. Henriksson.

of a single proper surfactant micelle is typically *ca.* 1 ms to 1 s and that such a micelle is effectively closed (*i.e.* has a fixed aggregation number) for time intervals $\leqslant 0.01 \, \mu s$.[8] Surface vibrations in the frequency range 10^{12}–10^{14} Hz essentially determine the intrinsic width of the interfacial zone and give rise to important contributions to the actual value of the micellar surface tension, γ.[9]

Typical microemulsion aggregates, on the other hand, are at present mostly considered as short-lived, highly fluid structures of undefined geometry.[10] Current theories on the stability and shape deformations of such aggregates are largely based on considerations of the bending free energy required to change the surface curvature from a certain 'natural' curvature, whereas the aggretate surface tension is generally supposed to be close to zero.[11,12] The experimental justification of this kind of theoretical approach is, however, indirect and rather weak. The present study shows that micelles and small emulsion droplets normally experience sizeable shape fluctuations for low (as opposed to ultralow) values of γ, *i.e.* when curvature-related free energies are unlikely to be of any importance.

THEORY

In this model the interior of the (closed) micelle and the surrounding liquid are considered to be frictionless incompressible fluids of densities ρ_1 and ρ_2, respectively, separated by a dividing surface with surface tension γ. The potential surface (free) energy, Φ, will then be, approximately,

$$\Phi = \gamma A = \gamma \int_0^\pi \int_0^{2\pi} \left[r^2 + \frac{1}{2}\left(\frac{\partial r}{\partial \theta}\right)^2 + \frac{1}{2\sin^2\theta}\left(\frac{\partial r}{\partial \varphi}\right)^2 \right] \sin\theta \, d\theta \, d\varphi \qquad (1)$$

where A is the surface of the distorted sphere and $r(\theta, \varphi)$ its radius as a function of θ and φ. Using the method employed by Lord Rayleigh when treating oscillations of a droplet in air[7] in a slightly generalized version, r is expanded in a series of spherical harmonics, $Y_{lm}(\theta, \varphi)$,

$$r(\theta, \varphi, t) = r_0 \left(1 + \sum_{l=2}^{l_{max}} \sum_{m=-l}^{+l} a_{lm}(t) Y_{lm}(\theta, \varphi) \right) \qquad (2)$$

where $l = 0$ and $l = 1$ are excluded for a closed micelle with a fixed centre of mass and where the meaning of the (time-dependent) radius r_0 will be clarified below. This yields the potential energy

$$\Phi = 4\gamma r_0^2 \left(1 + \frac{1}{8\pi} \sum_{l=2}^{l_{max}} \sum_{m=-l}^{+l} (-1)^m [l(l+1)+2] a_{lm} a_{l,-m} \right). \qquad (3)$$

Since the fluid inside the micelle is assumed to be incompressible we must have

$$4\pi R^3/3 = \int_0^\pi \int_0^{2\pi} \tfrac{1}{3}[r(\theta, \varphi)]^3 \sin\theta \, d\theta \, d\varphi \qquad (4)$$

where R is the radius of the undistorted micelle.

Insertion of eqn (2) shows that r_0 cannot be a constant if the micelle volume is to remain constant during the fluctuation. Neglecting low-order quantities the following relationship between r_0 and R is obtained:

$$r_0 \approx R \left(1 - \frac{1}{4\pi} \sum_{lm} a_{lm} a_{l,-m} (-1)^m \right). \qquad (5)$$

After taking account of this fact, the expression for the potential energy becomes

$$\Phi = 4\pi\gamma R^2\left(1 + \frac{1}{8\pi}\sum_{l=2}^{l_{max}}\sum_{m=-l}^{+l}(-1)^m[l(l+1)-2]a_{lm}a_{l,-m}\right). \tag{6}$$

In deriving this expression we have neglected the influence of the surface dilatation on γ, which should be permissible for the small-amplitude deformations studied here.

The fluid velocities inside ($i = 1$) and outside ($i = 2$) the micelle can be described by means of velocity potentials ϕ_i

$$\boldsymbol{v}_i = \nabla\phi_i \qquad (i = 1, 2) \tag{7}$$

if the motion is irrotational. If the liquids are assumed to be incompressible we have

$$\nabla^2\phi_i = 0 \qquad (i = 1, 2). \tag{8}$$

The question whether this assumption is valid at high vibrational frequencies has been answered, at least partially, by Brillouin.[13] By comparing the expression for the phase velocity of dispersive capillary waves on a planar surface calculated for an incompressible fluid with the corresponding expression calculated for a compressible fluid he concluded that the values become identical for frequencies where the phase velocity is considerably lower than the velocity of sound. This condition is fulfilled for the case under investigation. In addition, we observe that for potential streaming of an incompressible fluid the viscosity-dependent terms in the Navier–Stokes equation will vanish.

To obtain the kinetic energy, the potentials ϕ_1 and ϕ_2 are now expanded in the standard way:

$$\phi_1 = \sum_{l=2}^{l_{max}}\sum_{m=-l}^{+l}b_{lm}^{(1)}(t)r^l Y_{lm}(\theta, \varphi) \tag{9}$$

and

$$\phi_2 = \sum_{l=2}^{l_{max}}\sum_{m=-l}^{+l}b_{lm}^{(2)}(t)r^{-l-1}Y_{lm}(\theta, \varphi) \tag{10}$$

and the coefficients $b_{lm}^{(i)}$ are determined from the boundary conditions:

$$\frac{\partial\phi_1}{\partial r}(R, \theta, \varphi, t) = \frac{\partial\phi_2}{\partial r}(R, \theta, \varphi, t) = \frac{\partial r}{\partial t}(\theta, \varphi, t). \tag{11}$$

The kinetic energy is obtained from the following relations based on Green's theorem:

$$\begin{aligned}
K &= \tfrac{1}{2}\sum_{i=1}^{2}\rho_i\int v_i^2\,\mathrm{d}V = \tfrac{1}{2}\sum_{i=1}^{2}\rho_i\int(\nabla\phi_i)^2\,\mathrm{d}V \\
&= \tfrac{1}{2}\sum_{i=1}^{2}\rho_i\int[\nabla\cdot(\phi_i\nabla\phi_i)-\phi_i\nabla^2\phi_i]\,\mathrm{d}V \\
&= \tfrac{1}{2}\sum_{i=1}^{2}\rho_i\int_A(\phi_i\nabla\phi_i)\cdot\mathrm{d}\boldsymbol{A} \\
&= \tfrac{1}{2}R^2\sum_{i=1}^{2}(-1)^{i-1}\rho_i\int_0^{\pi}\int_0^{2\pi}\left(\phi_i\frac{\partial\phi_j}{\partial r}\right)_{r=R}.
\end{aligned} \tag{12}$$

Using the expansions for the ϕ_i this finally yields ($\dot{a}_{lm} \equiv da_{lm}/dt$ etc.)

$$K = \tfrac{1}{2}R^5 \sum_{l=2}^{l_{max}} \left(\frac{\rho_1}{l} + \frac{\rho_2}{l+1} \right) \sum_{m=-l}^{+l} (-1)^m \dot{a}_{lm}\dot{a}_{l,-m}. \tag{13}$$

Unfortunately, a_{lm} and $a_{l,-m}$ are not independent if $r(\theta, \varphi, t)$ is to be real. This is, however, easily remedied by forming the linear combinations

$$\alpha_{lm} = \frac{1}{2}[(-1)^m a_{lm} + a_{l,-m}]$$
$$\beta_{lm} = \frac{i}{2}[(-1)^m a_{lm} - a_{l,m}] \tag{14}$$

for all $m > 0$. In terms of these independent parameters we now obtain

$$\sum_{m=-l}^{l} (-1)^m a_{lm}a_{l,-m} = a_{l0}^2 + \sum_{m=1}^{l} (\alpha_{lm}^2 + \beta_{lm}^2) \tag{15}$$

from which we derive

$$\Phi = 4\pi\gamma R^2 + \tfrac{1}{2}\gamma R^2 \sum_{l=2}^{l_{max}} [l(l+1) - 2]\left(a_{l0}^2 + \sum_{m=1}^{l} (\alpha_{lm}^2 + \beta_{lm}^2) \right) \tag{16}$$

and

$$K = \tfrac{1}{2}R^5 \sum_{l=2}^{l_{max}} \left(\frac{\rho_1}{l} + \frac{\rho_2}{l+1} \right)\left(\dot{a}_{l0}^2 + \sum_{m=1}^{l} (\dot{\alpha}_{lm}^2 + \dot{\beta}_{lm}^2) \right). \tag{17}$$

The $(2l+1)$-fold degenerate vibrational frequencies, ω_l, are then easily obtained from Lagrange's equations of motion

$$\frac{d}{dt}\left(\frac{\partial K}{\partial \dot{\alpha}_{lm}} \right) = -\frac{\partial\Phi}{\partial\alpha_{lm}} \tag{18}$$

and correspondingly for β_{lm}. The result for the angular frequencies is

$$\omega_l = 2\pi\nu_l = \left(\frac{\gamma l(l-1)(l+2)}{[\rho_1 + \rho_2 l/(l+1)]R^3} \right)^{1/2} \tag{19}$$

with $l > 2$ since lower values of l imply a micelle size change ($l = 0$) or a displacement of the centre of gravity ($l = 1$). From eqn (19) the corresponding formula due to Lord Rayleigh [cf. ref. (7), (14) and (15)] is readily derived by putting $\rho_2 = 0$ for the exterior fluid.† Inserting the typical numerical values $\rho_1 = 0.8 \times 10^3$, $\rho_2 = 1.0 \times 10^3$ kg m^{-3}, $\gamma = 25$ mN m^{-1}, $R = 2.0$ and $l = 2$ in eqn (19) we get that $\nu_2 = 2.1 \times 10^{10}$ Hz.

As is rather obvious, there is also an upper limit to l since there must exist a lower limit to the wavelength of the surface waves beyond which the concept of capillary waves ceases to be meaningful. The magnitude of this lower limit, λ_{min}, in the case of planar surfaces of liquids has been discussed at length by Davis[17] and

† After this paper was submitted for publication it was brought to our attention that the general ($\rho_2 \neq 0$) capillary-wave frequency formula for a spherical droplet, eqn (19), has been obtained earlier by Henderson and Schofield[16] in connection with their work on the statistical mechanics of a liquid drop in contact with its own vapour. These authors also used methods which are rather similar to those applied here.

Weeks[18] among others. Accordingly, we may estimate the maximum number of surface capillary-wave modes, N, using the formula

$$N = 4\pi R^2 / \lambda_{min}^2. \tag{20}$$

As to the magnitude of λ_{min} there seems to exist general consensus [cf. ref (17) and (18)] that λ_{min} should be of the order of magnitude of 5 or 6 molecular diameters. The coefficient N is related to l_{max} in the following way

$$N = \sum_{l=2}^{l_{max}} (2l+1) = (l_{max}-1)(l_{max}+3) \tag{21}$$

whence

$$l_{max} = \sqrt{(N+4)} - 1 = 2\left(\frac{\pi R^2}{\lambda_{min}^2} + 1\right)^{1/2} - 1 \approx (2\pi^{1/2}R/\lambda_{min}) - 1. \tag{22}$$

In practice ν_{max} will be at most of the order of 10^{11} Hz. This corresponds to a phase velocity of ca. 260 m s^{-1}, which is much less than the velocity of sound inside and outside the micelle. In addition, $h\nu_{max}$ will be considerably less than kT, which ensures the validity of the equipartition theorem.

The contribution of the surface waves to the surface entropy and the surface tension is rather small. Referring to Weeks' calculation for planar surfaces (loc. cit.) we conclude that the former contribution will be less than k/λ_{min}^2 and the latter less than $kT/2\lambda_{min}^2$. We can therefore in most cases neglect these contributions.

Greater interest is, however, attached to the vibrational amplitude and surface dilatation, which may reach high values at low surface tensions. Since $\Phi = \gamma A$ the thermal average of the micelle surface area becomes

$$\langle A \rangle = \frac{1}{\gamma}\langle \Phi \rangle. \tag{23}$$

But according to the equipartition principle eqn (16) yields

$$\langle \Phi \rangle = 4\pi\gamma R^2 + NkT/2. \tag{24}$$

Thus

$$\langle A \rangle = 4\pi R^2 + NkT/2\gamma \tag{25}$$

and the surface dilatation or 'wrinkling' ratio becomes

$$1 + \kappa = \frac{\langle A \rangle}{4\pi R^2} = 1 + \frac{NkT}{8\pi\gamma R^2}. \tag{26}$$

Let us now introduce a 'characteristic' surface tension, γ^*, defined by

$$\gamma^* = \frac{NkT}{8\pi R^2} = \frac{kT}{2\lambda_{min}^2} \tag{27}$$

for each individual micelle. Then, the 'wrinkling' coefficient becomes

$$\kappa = \gamma^*/\gamma \tag{28}$$

which means that κ reaches comparatively high values when γ approaches γ^*.

Introducing the relation between r_0 and R, eqn (5), into eqn (2) and using the orthogonality properties of the spherical harmonics it is easy to show that

$$\overline{(r-R)^2} = \frac{1}{4\pi} \int_0^\pi \int_0^{2\pi} [r(\theta, \varphi, t) - R]^2 \sin\theta \, d\theta \, d\varphi$$

$$= \frac{1}{4\pi} R^2 \sum_{l=2}^{l_{max}} \left(a_{l0}^2 + \sum_{m=1}^{l} (\alpha_{lm}^2 + \beta_{lm}^2) \right). \tag{29}$$

The thermal average of this becomes

$$\sigma_r^2 = \langle \overline{(r-R)^2} \rangle = \frac{1}{4\pi} R^2 \sum_{l=2}^{l_{max}} \left(\langle a_{l0}^2 \rangle + \sum_{m=1}^{l} (\langle \alpha_{lm}^2 \rangle + \langle \beta_{lm}^2 \rangle) \right). \tag{30}$$

From the equipartition principle and eqn (16) we further conclude that

$$\tfrac{1}{2}\gamma R^2 [l(l+1)-2] \left\langle a_{l0}^2 + \sum_{m=1}^{l} (\alpha_{lm}^2 + \beta_{lm}^2) \right\rangle = (2l+1)kT/2. \tag{31}$$

Hence, the mean-square capillary-wave dispersion becomes

$$\sigma_r^2 = \langle \overline{(r-R)^2} \rangle = \sum_{l=2}^{l_{max}} \frac{(2l+1)kT}{4\pi\gamma[l(l+1)-2]} \tag{32}$$

or

$$\sigma_r^2/R^2 = \left\langle \left(\frac{r}{R} - 1 \right)^2 \right\rangle = \sum_{l=2}^{l_{max}} \frac{(2l+1)kT}{4\pi\gamma R^2[l(l+1)-2]} = \frac{2}{N} \frac{\gamma^*}{\gamma} \sum_{l=2}^{l_{max}} \frac{2l+1}{l(l+1)-2}. \tag{33}$$

For symmetry reasons, this is also equal to the capillary-wave dispersion at a single point of the surface. In addition to this there is, of course, also an intrinsic surface width.

The theory presented above is invalid for large-amplitude surface vibrations that, according to eqn (33), are predicted to occur at low values of γ. It may still be used, however, to obtain an estimate of the conditions when very large amplitude fluctuations are to be expected.

NUMERICAL CALCULATIONS

In our calculations we have put λ_{min} equal to 3.0 nm, which appears reasonable in comparison with the cross-section diameter of a straight hydrocarbon chain in the liquid-crystalline state (*ca.* 0.5 nm). With this choice of λ_{min} we obtain ($T = 300$ K) $\gamma^* = 0.230$ mN m^{-1}. It is thus evident that the surface wrinkling coefficient $\kappa = \gamma^*/\gamma$ (that is independent of R) becomes sizeable for $\gamma \lesssim 1$ mN m^{-1}.

The number of surface capillary-wave modes, N, increases with the micelle radius R as does l_{max}. This is shown in fig. 1. Note that only the d-type surface mode with $l = 2$ is operative for $R \leqslant 3.0$ nm.

The mean-square capillary-wave dispersion, σ_r/R, depends not only on γ but also in a complex way on R, as is evident from eqn (33). In fig. 2 σ_r/R is plotted against γ for different values of R. It appears that σ_r/R generally is $\leqslant 0.1$ for $\gamma > 10$ mN m^{-1} and that large shape fluctuations occur, particularly for small micelles, in the range below $\gamma = 1$ mN m^{-1}.
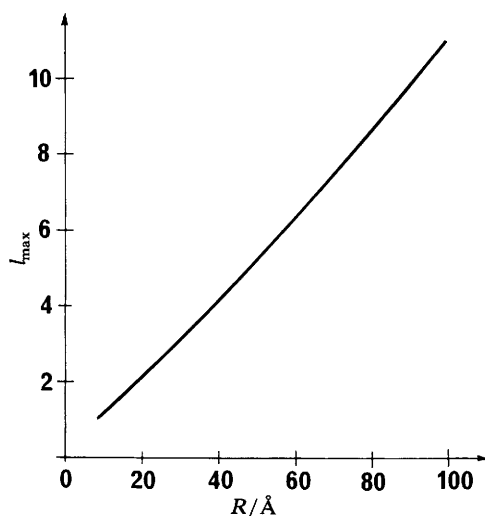
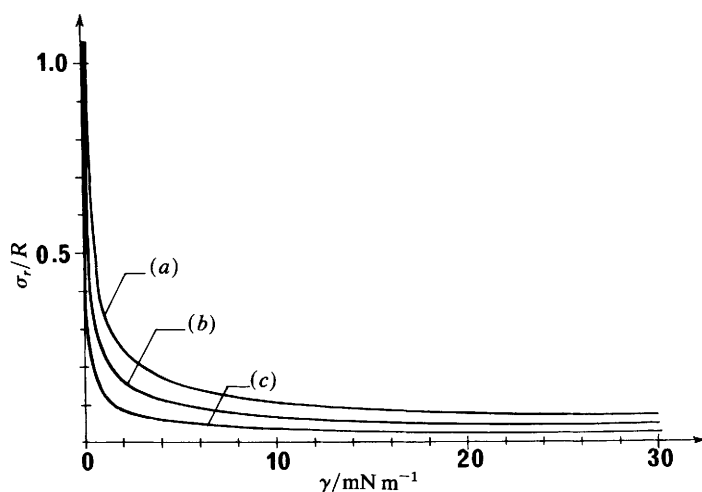**Fig. 1.** $l_{\max} = 2[(\pi R^2/\lambda_{\min}^2) + 1]^{1/2} - 1$ plotted as a function of R.

Fig. 2. Relative root-mean-square capillary-wave dispersion plotted as a function of γ with different values of R: (a) $R = 18.92$ Å, $l_{\max} = 2$, $N = 5$; (b) $R = 38.78$ Å, $l_{\max} = 4$, $N = 21$; (c) $R = 100.13$ Å, $l_{\max} = 11$, $N = 140$.

CONCLUSIONS

A significant result emerging from this theoretical investigation is that thermally excited shape fluctuations tend to become quite large for a spherical micelle when its surface tension, γ, is reduced to below *ca.* 1 mN m^{-1}. It is likely that values of γ of this magnitude can be approached when adding a medium-chain-length alcohol (cosurfactant) to a surfactant/water/oil system containing either o/w or w/o micelles, whereby typical microemulsions begin to form, as the hydrocarbon/water contact

area is diminished. It would thus appear that a spherical droplet with fixed shape is a poor point of departure when aiming at a model description of microemulsions.

According to the present calculations the transition to an extended interfacial zone, characterized by large values of κ and σ_r/R, between the dispersed and the continuous phases, takes place in a gradual fashion when γ is decreased to below *ca.* 5 mN m^{-1}. This behaviour is in good qualitative agreement with recent n.m.r. self-diffusion[10] and relaxation results,[19] which, in addition, indicate a very flexible aggregate structure and internal interfaces with a low degree of order in the true microemulsion region.

Some techniques used to probe the size and shape of micelles, such as neutron diffraction and light scattering, work on a timescale that is considerably shorter than 10^{-10} s. In such cases the shape fluctuations of (small) spherical micelles give rise to experimental effects which are usually attributed to anisotropy of the micellar aggregates. It is evident, however, from the results presented here that the (time and ensemble) average shape of the micelles investigated can still be spherical.

We should emphasize that only the effects of forces operating in tangential directions which contribute to the overall surface tension value, γ, are actually involved in our calculations. Forces operating in the direction normal to the interface appear to be of considerable importance for the resulting free energy required to form a micellar aggregate but they should presumably have a minor influence on the shape deformations of spherical micelles. This is to some extent in contrast to the situation with rod- and disc-shaped micellar aggregates for which the geometry-dependent hydrocarbon-chain conformation generates forces perpendicular to the interface that are probably decisive for the resulting mechanical stability [*cf.* ref. (5)].

In previous theories [*cf.* ref. (11)] it has often been presupposed that γ approaches zero for a microemulsion aggregate and that the interface bending free energy instead becomes essential. Recently Safran[12] has presented calculations on the size and shape fluctuations of spherical microemulsions in which only curvature contributions to the free energy are considered and constraints of constant total particle volume and surface area are imposed. Thus, according to Safran's model a variation of the number of open microemulsion particles (that requires a rather sluggish transport of surfactant molecules) takes place simultaneously with the fluctuations in shape. Complementary to Safran's approach, our aim here has been to provide a valid description of the rapid capillary-wave motions experienced by an ordinary surfactant micelle that is closed during the vibrations and for which evidence now available indicates values of γ in the range from *ca.* 5 to 30 mN m^{-1}. Under what conditions changes of the curvature-related free-energy contributions for a (spherical) micellar aggregate really have a significant influence on its thermal deformations, comparable with the $\gamma\Delta A$ term, is still very much an open question [see also ref. (20)]. However, there seem to be no well founded reasons to postulate that $\gamma = 0$ actually holds for a microemulsion aggregate or to impose a constant total surface area constraint and thus to rule out entirely the possible importance of interface stretching in the case of microemulsions.

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