Growth Kinetics of Fructose Crystals Formed by Contact Nucleation

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Despite the large number of recent secondary nucleation and growth rate studies with the sucrose-water system (Hartel et al., 1980; Kuijvenhoven and de Jong, 1982; Berglund, 1980; Gwynn et al., 1980; Shanks and Berglund, 1985), few data are available on the fructose-water system. Fructose is much more soluble in water than sucrose (Watanabe, 1978; Bates, 1942); for example, at 50°C, 100 g water can dissolve 662 g fructose as opposed to 260 g sucrose. This high solubility results in the viscosity of saturated aqueous fructose solution being much higher than that of saturated aqueous sucrose solution: at 50°C, 4,000–5,000 cp (4–5 $N \cdot s/m^2$) for fructose as opposed to 102 cp (0.102 $N \cdot s/m^2$) for sucrose (Watanabe, 1978). The viscosity leads to difficulties in the study of the crystallization of fructose and is probably one reason for the few kinetic studies of the system.

For the case of a continuous mixed-suspension, mixed-product-removal (MSMPR) crystallizer, Randolph and Larson (1971) have developed the population balance technique. Based on the assumptions of size-independent crystal growth, all crystals with equal growth rate (i.e., no growth rate dispersion), and all nuclei formed at a near-zero size, a semilogarithmic relation is predicted between crystal population density and size. When the model holds and a straight line is produced, the growth rate is determined from the slope and the nucleation rate is determined from both the slope and the intercept. However, evidence from continuous sucrose crystallization experiments (Hartel et al., 1980; Kuijvenhoven and de Jong, 1982), has shown that at lower crystal sizes ($<50 \times 10^{-6}$ m) orders of magnitude more crystals are present than are predicted by this relation. Therefore, one or more of the assumptions may be in error. The most likely violations are the nonzero birth size for nuclei and growth rate dispersion (Berglund, 1981).

The phenomenon of growth rate dispersion is a significant factor in the control of the crystal size distribution (CSD) in crystallizers. Two methods of modeling growth rate dispersion have been presented in the literature. The first, in which it is assumed that the growth rate of an individual crystal fluctuates in the course of time is referred to as the random fluctuation

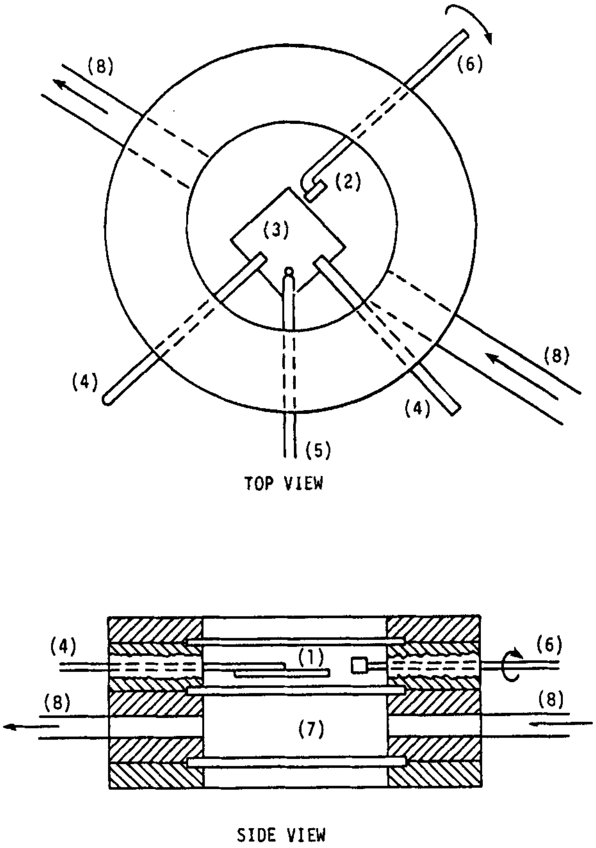

Figure 1. Nucleation cell.

1. Solution chamber
2. Parent crystal
3. Glass cover slip where parent crystal is placed
4. Support rods for glass cover slip
5. Thermistor
6. Movable rod holding parent crystal
7. Constant-temperature water chamber
8. Water inlet, outlet

(RF) model (Randolph and White, 1977). In the second, based on the contact nucleation studies of Berglund (1981), Berglund and Larson (1982), and Ramanarayanan et al. (1982), it is assumed that an individual crystal has an inherent, constant growth rate, but different crystals have different inherent growth rates. This model will be referred to as the constant crystal growth (CCG) model.

Gwynn et al. (1980) studied contact nucleation in the sucrose-water system and confirmed that contact nucleation is the primary source of new particles. In addition, it was found that contact nuclei of sucrose have an initial size distribution, not zero size as required by the MSMPR crystallizer model. Shanks and Berglund (1985) observed size-independent growth and compliance with the CCG model for contact nuclei in the sucrose-water system. Furthermore, they postulated that curvature in semilogarithmic population density vs. size plots from continuous sucrose crystallization is probably due to growth rate dispersion.

Table 1. Conditions and Number of Nuclei Analyzed for Photomicroscopic Experiments with Fructose-Water System

Run No.	Supercooling °C	Temp. °C	No. Nuclei Analyzed
1	1	30	16
2	3	30	12
3	5	30	11
4	7	30	17
5	1	40	11
6	3	40	12
7	5	40	12
8	7	40	12
9	3	50	20
10	5	50	15
11	7	50	13
12	9	50	14

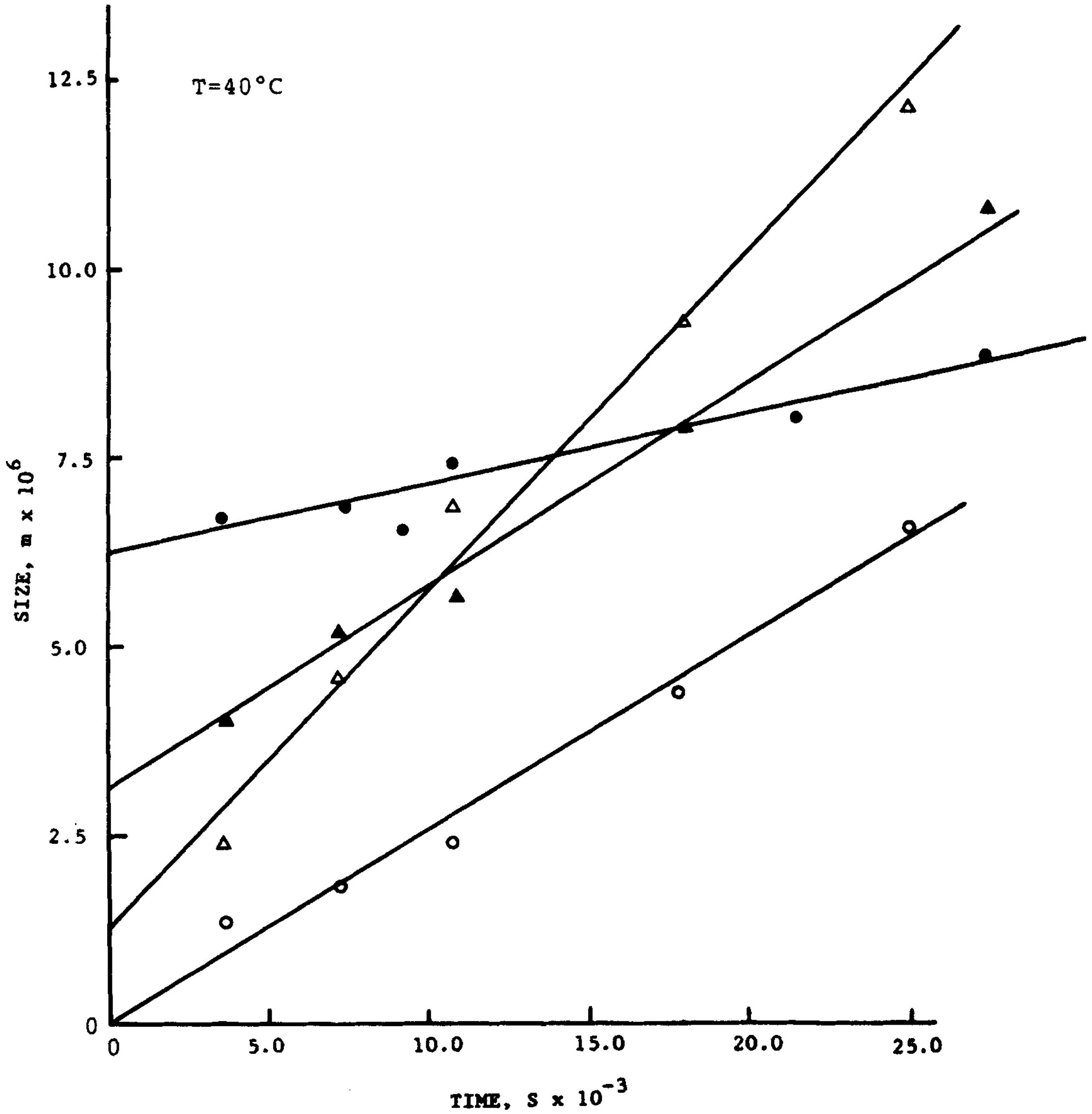

Figure 2. Examples of size vs. time data for contact nuclei of fructose formed and grown at 40°C.
Each line corresponds to a single crystal.

Since fructose is a monosaccharide constituting half of the sucrose molecule, it is reasonable to consider that similar phenomena may exist with respect to nucleation and growth in the two systems. It is the objective of this work to perform photomicroscopic experiments on the fructose-water system to study these nucleation and growth characteristics.

Experimental Apparatus

The experimental apparatus and techniques were the same as those used for the aqueous sucrose system by Shanks and Berglund (1985). A schematic diagram of the cell with a description of features is shown in Figure 1. The experimental conditions and the number of nuclei analyzed are given in Table 1.

Data Analysis

The raw data obtained from each experiment consisted of a series of photographs. The negatives of the photographs were projected to enlarge them for measurement. An image analyzer was used to determine the area of each crystal in the enlargement. The characteristic size was taken as the equivalent circular diameter, which can be transformed to the geometric mean size by multiplying by $\sqrt{\pi}/2$. The sizes were then plotted against time with the slope equal to mean growth rate and intercept equal to apparent initial size.

Results and Discussion

Figure 2 shows examples of size vs. time plots for some individual crystals at 40°C. It is evident, and confirmed by high correlation coefficients, that a linear relation exists between the size and time. Since the slope of the line is equal to growth rate, these plots imply a single, size-independent growth rate. The lines also have different slopes, indicating a distribution of growth rates, i.e., growth rate dispersion. Furthermore, the variation in intercept, which corresponds to an initial size distribution (Gwynn et al., 1980), is apparent. In Figure 3, the growth rate is plotted against the apparent initial size for each nucleus formed and grown at 40°C. Little correlation is present, as evidenced by the large amount of scatter. This indicates a distribution of apparent initial sizes and a distribution of growth rates. Similar plots have been observed for the data taken at 30 and 50°C. These results indicate that the CCG model describes this system.

Figure 4 shows the relationship between mean growth rate and relative supersaturation ratio at the different temperatures studied. The solubility data were taken from circular C440 of the National Bureau of Standards (Bates, 1943).

Since the mean growth rate can be expressed in terms of a power law model and the temperature dependence of the kinetic model can be analyzed in terms of the Arrhenius relation, the mean growth can be written as

$$\bar{G} = A \exp(-E_G/RT)S^n \qquad (1)$$

The data in Figure 4 were fitted to Eq. 1 with the following result,

$$\bar{G} = 3.97 \times 10^{-3} \exp(-25.6/RT)S^{1.25} \qquad (2)$$

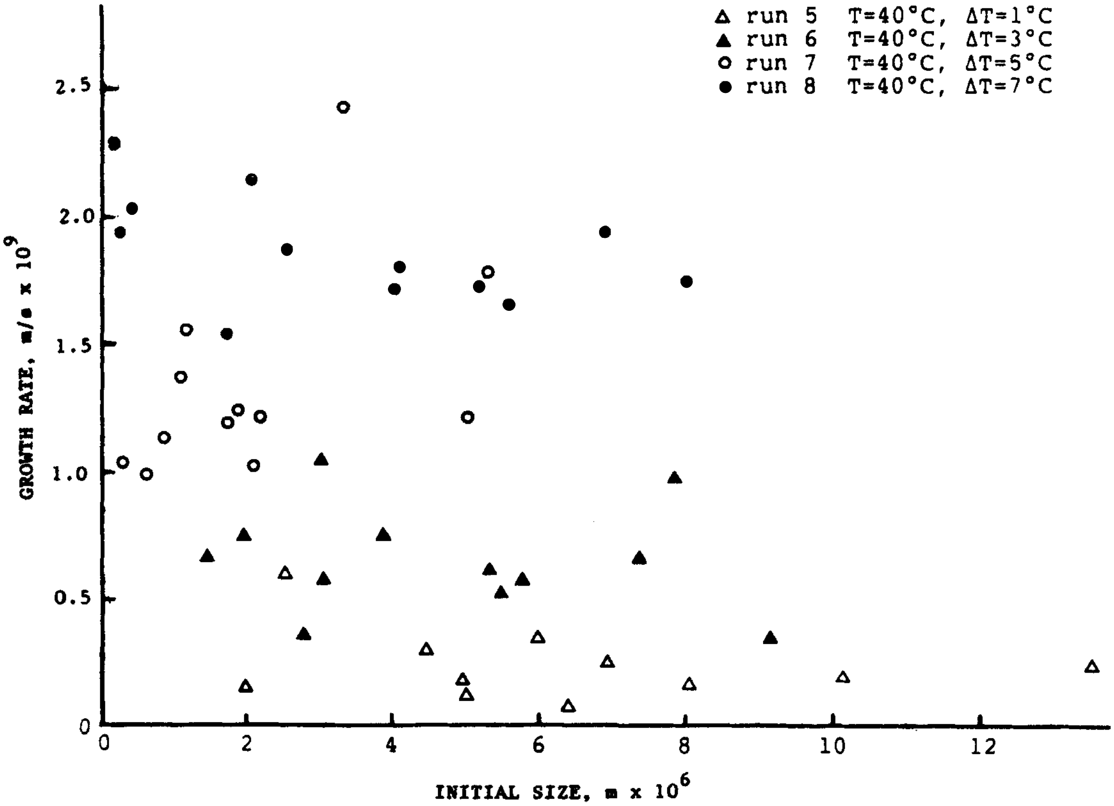

Figure 3. Growth rate vs. apparent initial size for contact nuclei of fructose formed and grown at 40°C.

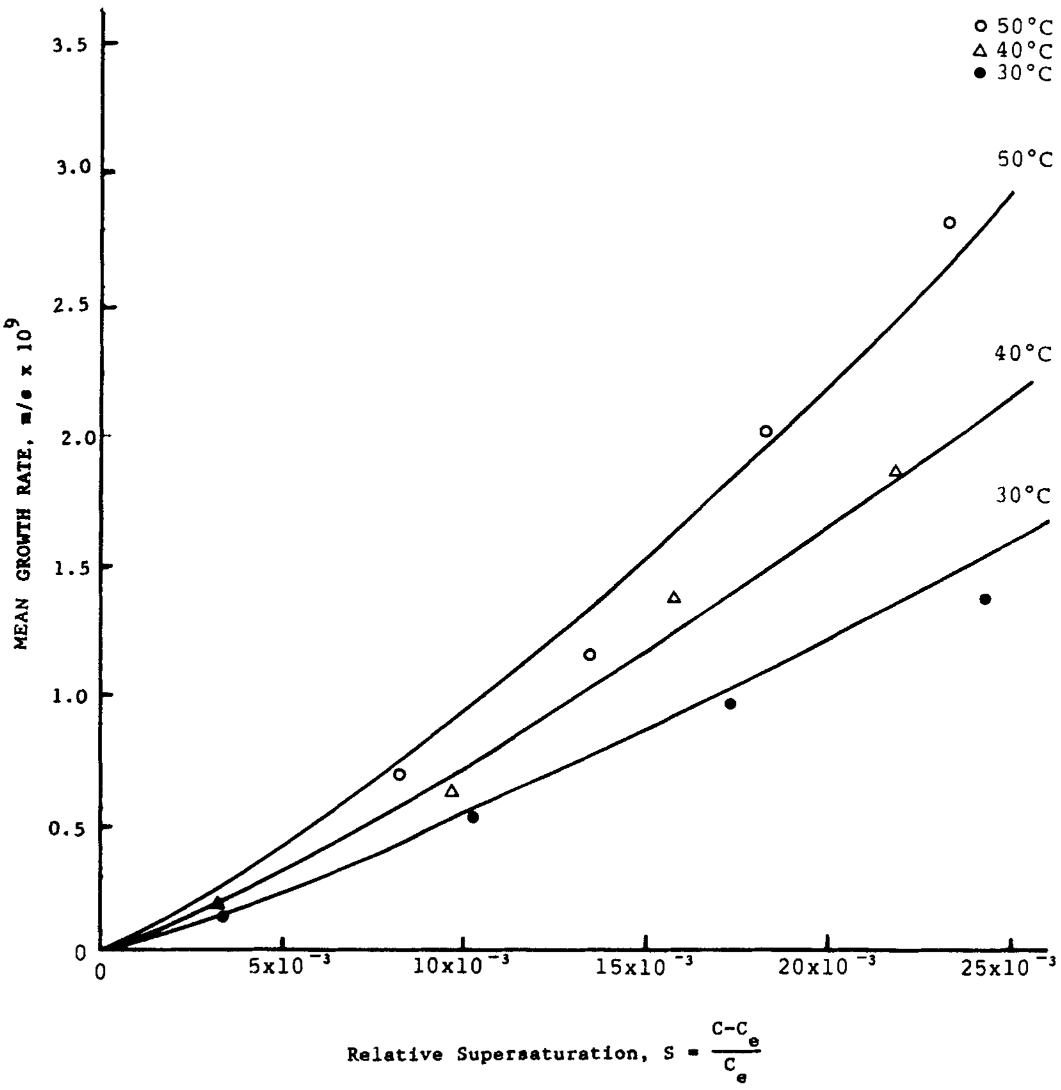

Figure 4. Mean growth rate vs. relative supersaturation for contact nuclei of fructose.
Each symbol represents a mean value for the number of nuclei analyzed, Table 1.

Upon comparison to sucrose growth rates, it is apparent that the rate for fructose is much slower. The mass transfer engineering crystal growth model presented by Ohara and Reid (1973) predicts a value of one for a volume-diffusion controlled process. The Burton-Cabrera-Frank (BCF) surface diffusion and dislocation model (Burton et al., 1951) predicts a value of 1 for n at high supersaturation and value of 2 at low supersaturations. For the range of relative supersaturations studied, S is small (0.0032–0.024); n would be expected to have the value of 2 in a surface-integration controlled process. However, n was found to have the value of 1.25, which may indicate that both volume diffusion and surface integration are important. This is further supported by the value of activation energy.

Smythe (1967) stated that the activation energy for the volume diffusion process in sucrose crystal growth is between 29.3 and 37.7 kJ/mol. In this work an activation energy of 25.6 kJ/mol was obtained for the growth rate. Since the exact value of the activation energy for the volume diffusion of fructose solution is not available in the literature, it is difficult to determine whether the crystal growth is diffusion-controlled or surface-integration controlled. However, for a purely diffusion-controlled process no growth rate dispersion should be observed, since growth rate dispersion is thought to be a surface phenomenon. Since 25.6 kJ/mol is near the range of 29.3–37.7 kJ/mol, it can be expected that both volume diffusion and surface integration play important roles here. This also suggests that growth rate dispersion can be observed in systems when volume diffusion is thought to dominate.

To estimate the parameters of the growth rate distribution, the variance of growth rates was calculated at each experimental condition. To correlate the growth rate distribution data, a power law expression is proposed to exist between the variance of the growth rate distribution and mean growth rate. The result of fitting the data is

$$\sigma_G^2 = 1.01 \times 10^{-7}\,\bar{G}^{1.35} \tag{3}$$

When the above result is compared with $\sigma_G^2 = 2.71 \times 10^{-3}\,\bar{G}^{1.74}$ for the sucrose-water system (Berglund and Murphy, 1986)—

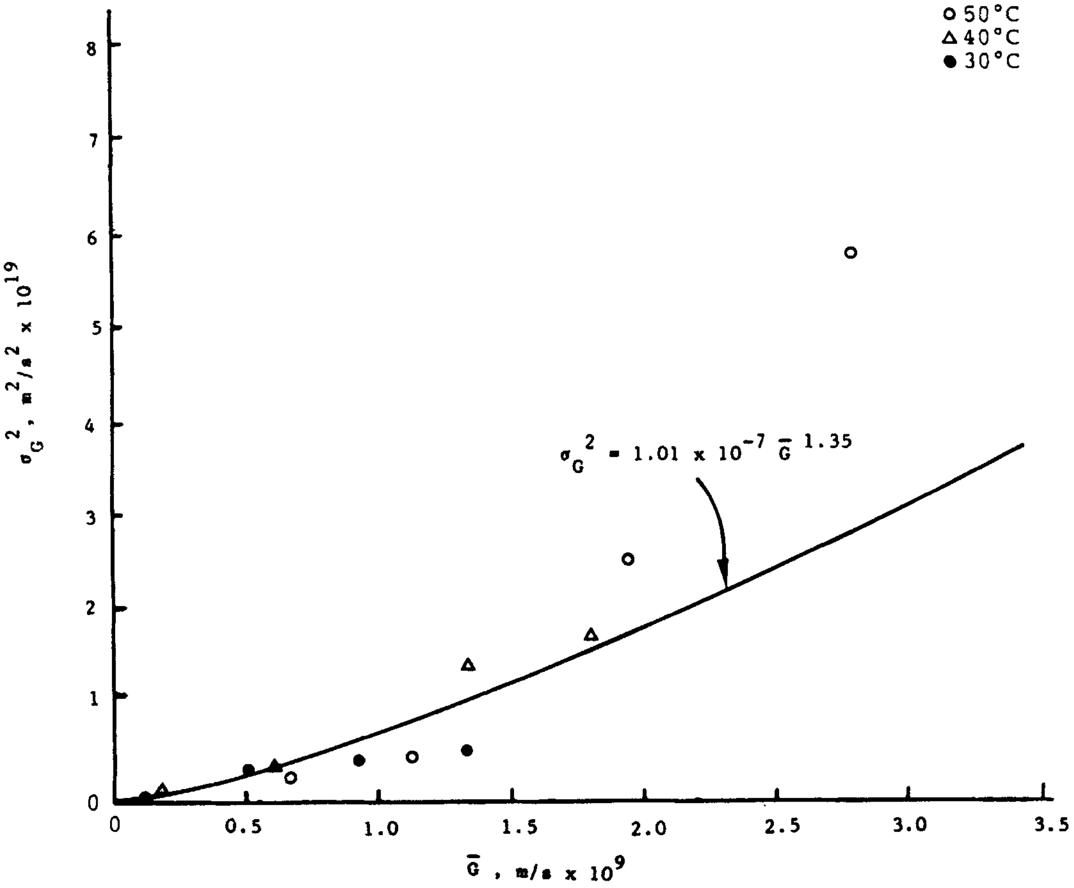

Figure 5. Variance of growth rate distribution vs. mean growth rate for contact nuclei of fructose.

for which it has been shown that growth rate is not mass-transfer limited—it is evident that the variance of the growth rate distribution in the fructose-water system is smaller than that in the sucrose-water system. However, there is still similarity between these two systems, since the exponents are greater than one for both systems.

Larson et al. (1985) have developed an expression based on the CCG model that relates the CSD from a MSMPR crystallizer to the growth rate distribution. Even a limited knowledge of only the mean growth rate and the variance of growth rate distribution (as determined in this study) permits an approximation of the expected CSD. Furthermore, the same approach can be applied to predict the resulting CSD when the model is extended to a cascade of MSMPR crystallizers. This is the subject of a subsequent paper.

Acknowledgment

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Notation

A = frequency factor, m/s
C = Concentration, g fructose/100 g solution
C_e = saturation concentration, g fructose/100 g solution
E_G = activation energy, kJ/mol
$\bar{G}$ = mean linear crystal growth rate, m/s
n = growth rate order
R = ideal gas constant, 8.3143×10^{-3} kJ/mol · K
S = relative supersaturation = $(C - C_e)/C_e$
T = temperature, K
σ_G^2 = variance of growth rate distribution, m²/s²

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