

THE ASYMMETRY OF ORGANIC AEROSOL FISSION AND PREBIOTIC CHEMISTRY

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Abstract. We examine the prebiotic applicability of our recent analysis of the fission of an atmospheric aerosol particle coated with an organic film. The fission is made possible by the free energy change upon compression of the exterior monolayer film on the parent particle, which overcomes the increase in surface area associated with the production of two spherical daughter particles. Asymmetric division into a larger and a smaller particle becomes possible following surfactant film collapse. The size of the airborne parent particle is determined by the balance between aerodynamics and gravity, while the ratio of the radii of the daughters is determined by the compression characteristics of the amphiphilic molecules comprising the parent film. For an Earth atmosphere of one bar surface pressure, the larger and smaller daughters have the sizes of a single-celled bacterium and of a virus respectively. Chemical differentiation between the daughters is possible.

Keywords: aerosol fission, bacteria, prebiotic, virus

1. Introduction

Recent advances in field instrumentation have shown that individual aerosol particles may have organic content of ~10% in the marine boundary layer (Middlebrook *et al.*, 1998) and as high as ~50% in the upper tropical troposphere, by mass (Murphy *et al.*, 1998). While it is difficult to explain the high organic content in terms of bulk solubility via Henry's Law coefficients, it can be reconciled by means of an inverted micelle model (Gill *et al.*, 1983; Ellison *et al.*, 1999). Recently, experimental support for the presence of long chain carboxylic acids as the main constituents of the outer film on contemporary marine aerosols has been reported (Tervahattu *et al.*, 2002a) – in particular, palmitic, oleic and stearic acids (Tervahattu *et al.*, 2002b). In the present atmosphere, these acids are of course of biological origin (Liss *et al.*, 1997). Organic aerosols of marine origin have been suggested as sites at which life could have originated (Shah, 1970; Lerman, 1996), while the inverted micelle model of atmospheric aerosols has been discussed as a correctly sized and structured prebiotic chemical reactor (Dobson *et al.*, 2000); it was also pointed out that there was a potentially causal connection between organic aerosols and climate, via their effect on the radiative balance. Woese (1979) argued that a con-



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tainer would have been necessary to transform geochemistry into biochemistry, and suggested superheated water droplets in high, hot clouds prior to the formation of liquid oceans. Morowitz (1992) also made a strong case for a 'cells first' evolution. Recently, we have performed a theoretical thermodynamic analysis (Donaldson *et al.*, 2001) of the question as to whether aerosols can divide in addition to their long-known ability to coagulate (e.g., Pruppacher and Klett, 1998).

There can be little doubt that aerosols would have been generated at the pre-biotic air-sea interface. The planet would have been rotating, with its axis tilted; the resulting heating gradients combined with the Coriolis force would have driven surface winds which in turn would have produced whitecaps. The aerosols would have been produced as they are now by the jet and cap mechanism during bubble bursting (Mason, 1954; Blanchard, 1964).

Coagulation and division have been proposed as a primitive means by which protocells could replicate without the need for coded molecular instruction mechanisms of the sort which operate in current life (Luisi, 1996; Norris and Raine 1998; Dobson *et al.*, 2000), and have been considered in a synopsis of a program to synthesize life (Szostak *et al.*, 2001). Here we briefly recapitulate the free energetics of aerosol coagulation and division, and point out that replication by symmetrical fission of a parent particle is not expected thermodynamically, but that asymmetric fission is enabled by film compression, resulting in one bacterially-sized and one virally-sized daughter particle.

2. Aerosol Fission

Two spherical aerosol particles can coagulate to form one spherical particle because the surface energy is thereby minimized; surface energy per unit area is equivalent to surface tension, γ , and the area of the single sphere is always less than the sum of the areas of the two coagulating particles. These arguments preclude the reverse process, spontaneous fission, for homogeneous liquid particles, for example of water and aqueous solutions. However, the presence of an organic film will lower the surface tension, and by virtue of the compression energetics associated with the film's 2D analogues of gaseous, liquid and solid states embodied in Figure 1, fission becomes possible.

Figure 1 illustrates a 2D isotherm for a film of stearic acid (the C₁₆ n-isomer carboxylic acid) upon water. After compressing such a film from a highly expanded state (large surface area per molecule) to point X, corresponding to an area of 15.3 Å² per molecule, the film is not further compressible and will collapse, forming disordered multiple layers prior to entering a separated bulk phase. The addition of more stearic acid molecules at point X will result in film collapse at point Y without further change in surface pressure or droplet size. The general shape of the isotherm at film collapse is typical for alkanolic acids in the C₁₂–C₁₆ range (Petrov *et al.*, 1999); the exact value of the area per molecule at this point is

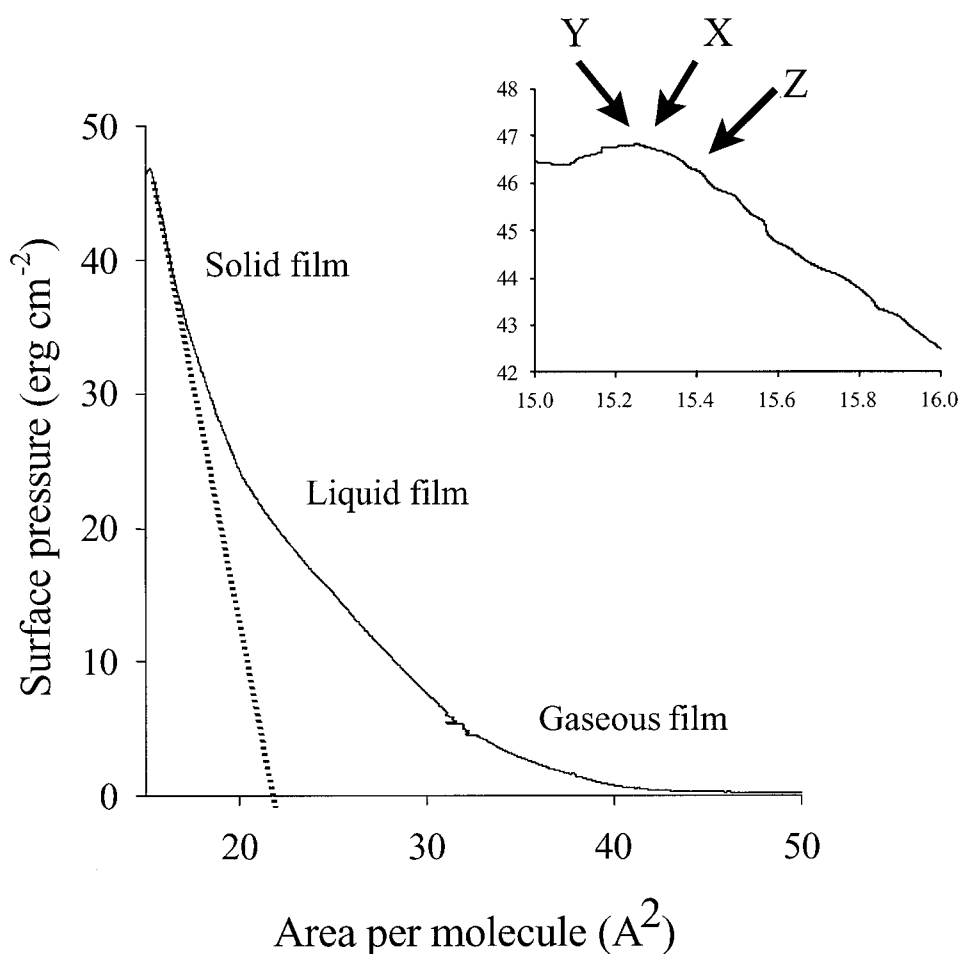


Figure 1. An isotherm (293 K) of stearic acid on water measured in the Vaida laboratory using a Langmuir trough. The inset shows the region near film collapse; the labels X, Y and Z are referred to in the text. The area per molecule at zero film pressure, 22 \AA^2 , is obtained by extrapolating the solid film part of the isotherm back to the abscissa and is in agreement with literature values. The area per molecule at film collapse (inset, point X) is dependent upon the rate of film compression.

dependent upon several factors, including the rate at which the film is compressed. It is about 18 \AA^2 when the compression rate is low enough that kinetic effects are minimal, but note that the division (and hence the compression) must be rapid and irreversible (Donaldson *et al.*, 2001). We now make a theoretical argument in which an aerosol particle is allowed to divide, irreversibly and instantaneously, into two. There will have been an irreversible expansion from Y to Z on the isotherm, with the work of compression being equal to the area under the curve between these points. The creation of two particles by fission will have increased the surface

area and relieved the need for film collapse. Donaldson *et al.* (2001) show that the condition for division is

$$\gamma_1 + \gamma_2 K^2 < \gamma_P (1 + K^3)^{\frac{2}{3}},$$

where γ_1 , γ_2 and γ_P are the surface tensions of the daughters 1 and 2 and of the parent, respectively. $K = r_2/r_1$ is the ratio of the radii of the daughters and $K < 1$. As Dobson *et al.* (2000) have pointed out, the radius of a typical aerosol particle having the maximum residence time in the Earth's atmosphere is determined by Stokes's Law, the balance between aerodynamic drag and gravitational subsidence, and is of order 1 μm . Using representative numerical values, Donaldson *et al.* (2001) obtain limiting cases $K = 1$ and $K = 0.1$

$$\gamma_1 + \gamma_2 < 1.59\gamma_P \quad (K = 1)$$

and

$$\gamma_1 + 0.01\gamma_2 < 1.001\gamma_P \quad (K = 0.1).$$

The case $K = 1$ is clearly unlikely; it would require the surface tensions of the daughters to be much less than that of the parent. However, for the case $K = 0.1$ division will increase the total surface area by 1%, equivalent to an energy value which can be surmounted if the parent has a compressed film coating. Near this limit, in the Earth's atmosphere, the implication is that the larger daughter is bacterium-sized, and the smaller daughter is virus-sized.

The asymmetric division just described gives no indication as to whether the small daughter finishes up inside or outside the larger daughter. The above reasoning thus in principle provides a thermodynamically feasible, one-step process for the production of a micron-sized particle with a much smaller particle (order of magnitude less in diameter) either exterior to it or interior to it. An obvious question at this juncture is if chemical differentiation between these two daughters is possible. Examination of this idea can only follow a discussion of chemical heterogeneity, both in the film and the polar interior.

3. Chemical Differentiation by Selective Fission

The surface of the planet is chemically heterogeneous now, at both land and sea surfaces, and was in the prebiotic era (Williams and Fraústo da Silva, 1996). The processes forming alkanes, and their functionalized derivatives resulting from reaction with atmospheric OH (Tuck, 2002) could have produced a range of carboxylic acids and amino acids. Possible sources of monomers and starting materials include, for example, lightning discharges or solar UV radiation (Miller, 1998) and synthesis in or near hydrothermal vents (Shock *et al.*, 1995; Simoneit, 1995; Huber

and Wächtershäuser, 1998; Cody *et al.*, 2000). If the prebiotic source of these was meteoric or cometary rather than endogenous, the chemical heterogeneity would still have been evident (Cronin, 1998). A role for containers formed by self-assembly of amphiphilic molecules has also been argued (Deamer, 1997). There is experimental evidence for the formation of lipid rafts in membrane monolayers (Dietrich *et al.*, 2001), enabled by 2D diffusion in the film and favoured by the self-assembly of like species. Given this, it is possible that chemical differentiation could occur in the surface layers of the daughter particles formed by aerosol fission: surface energy would be minimized if the smaller particle had the maximum amount of the component domain with the lowest surface tension. The ability of reverse micelles in aqueous solution to act as hosts for proteins and small molecules has been reviewed by Robinson and co-authors (Luisi *et al.*, 1988).

Chemical differentiation of polypeptides or proteins between the bulk and the surface film is possible, based upon the experimental studies of protein surface activity by Razumovsky and Damodaran (1999). They found empirically that rigid and inflexible globular proteins were not able to reduce the surface tension of water even at saturated monolayer coverage, and obtained a relationship between a measure of their compressibility or flexibility (ability to unfold) at the air-water interface with their surface activity (ability to lower surface tension). On that basis, in the parent particle, we argue that the more folded, globular polypeptides and proteins would be found in the bulk core, while the more flexible and therefore surface active ones would be found in the film. Upon division, the most flexible polypeptides might have formed the outer film of the smaller daughter, driven by the need to minimize the surface free energy. Thus the most surface active peptides would encase the much smaller volume; it would be interesting to perform experiments to see if any polynucleotides or nucleic acids present tended to occupy this smaller volume by virtue of the efficient space-filling properties of α -helical molecules. If so, the larger daughter would consist of more complicated molecules in an aqueous core contained by a mixed film of carboxylic acids and flexible proteins, while the smaller one consisted of a flexible protein coat surrounding nucleic acids. Experimental tests of such partitioning mechanisms seem possible.

The existence of homomolecular or mixed domains in the surface films has further implications. The boundaries between such domains might have potential as reaction sites, a possibility considered in the next section.

4. Reaction at Interfaces

It has been proposed (Ellison *et al.*, 1999) that the surfactant molecules in an inverted micelle aerosol particle will be subject to reaction with gas phase OH in the current atmosphere. This suggestion has recently been supported by laboratory investigation (Bertram *et al.*, 2001), where a film of palmitic-stearic acid was shown to react with OH in a flow reactor at a rate up to 0.5 of the collision

frequency. This result means that it is likely that any hydrocarbons such as alkanes and alkenes on the ocean surface would be oxidized by this mechanism, particularly after they were incorporated into aerosols by bubble-bursting (Dobson *et al.*, 2000; Tuck, 2002). This would have led to the production of alcohols, aldehydes and acids in the prebiotic atmosphere, which would have contained OH by virtue of UV irradiation of atmospheric water vapour. The absence of ozone in the prebiotic atmosphere would have allowed photodissociation of water to lower altitudes than at present. It is open to experiment to see if long chain carboxylic acids can emerge via such reactions on films. It would seem to be plausible, since despite the greater statistical and thermodynamic probability of branched chain alkanes, experiments in which R_1 and R_2 in $R_1R_2CHCOOH$ were systematically varied (Ställberg-Stenhagen and Stenhagen, 1945) do suggest that straight R_1 and R_2 pack better than branched variants in films compressed to the ordered liquid or solid phases. There appears to be little or no experimental work on the polymerization of amino acids to form peptides in Langmuir films, or of nucleotides to form nucleic acids in similar circumstances. Haselmann and Laustriat (1973) observed minor production of melanin, a pigment, when the amino acid tyrosine was exposed to 254 nm light.

The molecular scale environment in an ordered liquid or solid phase in a two dimensional film of mixed composition could offer alignment and orientation possibilities at domain or raft boundaries. The water-free environment in the film would make condensation reactions to produce biopolymers easier than in the bulk aqueous phase. Domain boundaries could have very large lengths on scales of 10^{-9} to 10^{-6} m, rather like the fractal scaling of a coastline; percolation theory treatments (Dewey, 1999) of the mosaic model of cell membranes support this possibility. Adam and Delbrück (1968) pointed out the acceleration of reaction rates associated with a reduction in dimensionality. If (there appears to be no experimental evidence for or against) the smaller daughter during fission was formed with an outer coat of peptides, while the larger daughter was formed with primarily long chain carboxylic acids on its exterior, it would have a structural similarity to the present day protein coats on viruses and the lipid walls of single-celled bacteria. Experimental tests of these ideas are an attractive possibility.

We will look briefly at the question of reaction times and cycles for aerosols forming at and re-entering the air-sea interface. If we take the oldest ocean-related material in the geological record (zircons), their age is 4.40 Gy (Mojzsis *et al.*, 2001; Wilde *et al.*, 2001). The age of the oldest fossil bacteria is 3.56 Gy (Schopf, 1998). Therefore the upper limit of the time period in which life originated is 840 My; it could of course have been much less and probably was because of the late meteoric bombardment. During this period, there would have been up to $\sim 10^{14}$ aerosol cycles between the ocean and the atmosphere. Adopting, *faute de mieux*, Dyson's (1985, 1999) toy model in which 10^{10} droplets each containing 2000 to 20 000 reactive molecules of 8–10 polymerizing species of monomer produced one transition from randomness to self-catalytic order in 10^3 reaction times,

we can make an estimate of the number of life-generating opportunities. In the atmosphere from the surface to 16 km, roughly the height of the tropopause, there would be of order 10^{17} volumes each containing Dyson's minimum population. These enormous, varied and repeatedly cycled populations would have offered up to as many as $\sim 10^{31}$ opportunities for a successful population to emerge, probably after many failures by initially successful populations. The general point remains even if the 840 My is reduced by 3 orders of magnitude or more.

5. Summary

Based upon developments from atmospheric observations, a model has been proposed in which inverted micelles in the prebiotic atmosphere were the chemical reaction vessels in which life could have evolved (Dobson *et al.*, 2000). In this article, we have explored the nature of coagulation and division of such aerosols. While coagulation is a known process in atmospheric aerosols, division has long been discounted on energetic grounds. Here we have used the results from a theoretical thermodynamic analysis of a typical atmospheric aerosol particle with an organic film casing to show that division could occur; it is the result of the energetics of film compression, and must be asymmetric. Typical numbers yield the result that the larger daughter is bacterially sized and the smaller daughter is virally sized; both are produced in a single step. Virally-sized and bacterially-sized particles could share a common origin in a simple division mechanism in organic film-encased aerosols; chemical differentiation of the film is possible upon fission.

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