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1. INTRODUCTION

For more than 50 years a common theme in many warm rain cloud microphysical studies has been the inability of cloud models to explain the breadth of droplet spectra observed in natural clouds. The comparison between observations and models is difficult because droplet spectrometers are not free of error and also because of artifacts that are often an integral part of numerical models. Nevertheless, the plethora of studies on the subject tends suggest that the disparity in spectral breadths is likely a real one (Hudson and Yum 1997). A variety of mechanisms might account for this disparity including entrainment mixing (Baker et al., 1980), vortex structures that create inhomogeneous spatial distributions of droplets (Shaw et al., 1998), longwave cooling (Roach, 1976), aqueous chemistry (Zhang et al., 1998), and giant CCN (radii $> \approx 1 \mu\text{m}$) that broaden spectra through collision-coalescence.

This paper does not dispute these works, nor does it attempt to ascertain their relative importance. Instead it focuses on an alternative mechanism which has not been widely considered. The main idea is that some amphiphilic organic compounds (that we will term film-forming compounds, or FFCs) can form compressed films on the surface of droplets, and that this coating may inhibit droplet growth for long enough that some fraction of droplets grows in conditions of relatively high supersaturation and they achieve larger sizes than they would have, had the entire population of drops been growing simultaneously. By the time the film on the haze droplets is reduced to less than a complete monolayer, and these drops can grow freely, the size spectrum is significantly broader than that achieved in FFC-free conditions.

A few, limited studies have examined the potential effects of surface films on cloud formation (Podzimek and Saad, 1975; Derjaguin et al., 1985). They suggest that a more rigorous exploration of the conditions under which FFCs might have an effect on drop spectral evolution is in order. The current study includes a detailed analysis of model results, and attempts to understand the implications for drop spectral broadening and climate. Further details can be found in Feingold and Chuang (2002).

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2. EVIDENCE FOR FFCs

It has been argued that “organic films are probably common on atmospheric aerosol particles” (Gill et al. 1983). The existence of compressed films on sea salt droplets was deduced by Blanchard (1964). Laboratory experiments have shown that compressed surface films of certain organic compounds can retard evaporation and/or condensation of water from flat surfaces although the mechanism for such retardation remains unconfirmed (for reference list, see Feingold and Chuang 2002).

Studies of a man-made fog with and without cetyl alcohol (a commonly used substitute for FFCs) show reduced formation and dissipation rates when the alcohol is added. Bigg et al. (1969) conducted field experiments which yielded results that are consistent with reductions in fog formation by using a mixture of cetyl alcohol and octadecanol. Bigg (1986) reported that the formation of droplets in a CCN counter exhibited a time dependence; sometimes a cloud of droplets was formed quite quickly (≈ 1 to 2 s) while on other occasions up to 30 s was required. This suggests that the rate of condensational growth of some particles is substantially reduced, possibly due to the presence of surface films.

2. MODEL

An adiabatic parcel model adapted from Feingold and Heymsfield (1992) is used. The model calculates water vapor uptake by particles, activation, and condensation growth for a steady updraft. Because there is some evidence that spectral broadening may exist within adiabatic cores of cumulus clouds the adiabatic framework would seem to be a reasonable starting point. In the current work the vertical velocity, w is assumed to vary over the range $20 \leq w \leq 300 \text{ cm s}^{-1}$. The thermal accommodation coefficient is assumed to be unity. The particles are assumed to be partially soluble and composed of 50% ammonium sulfate (by mass) and 50% of an unspecified nonhygroscopic material, some fraction of which is FFC (see below). Aerosol size distributions are parameterized by a lognormal function and defined by three parameters: r_g , the median dry radius; σ , the geometric standard deviation; and N_a , the total particle concentration. These parameters have been varied over a broad range of parameter space to represent a variety of scenarios: $0.03 \mu\text{m} \leq r_g \leq 0.10 \mu\text{m}$; $50 \text{ cm}^{-3} \leq N_a \leq 1000 \text{ cm}^{-3}$; $1.3 \leq \sigma \leq 2.2$. The spectra are represented by 100 discrete sizes and

the growth of these particles is calculated on a moving grid to eliminate numerical diffusion. The spectra are defined in the range $0.01 \mu\text{m} < r < 1 \mu\text{m}$ and thus do not represent giant CCN.

a. Modeling the effect of FFCs on α

The condensation coefficient α is assumed to be 0.042 (e.g., Chodes et al. 1974) for all simulations for which particles are assumed to be free of FFCs. We simulate the effect of FFCs as a step increase in α from a small number ($\alpha=10^{-5}$), when the haze particle is covered by enough molecules of FFC to constitute a monolayer, to $\alpha=0.042$ when the number of molecules of FFC is insufficient to comprise a complete monolayer. For the assumed FFC, cetyl alcohol (1-hexadecanol, molecular weight 242), this step occurs when the surface area occupied per cetyl alcohol molecule is $>$ than 22 \AA^2 .

b. Distribution of the FFC mass among particles

The total mass of FFC is prescribed as a percentage of the total aerosol mass; values used here range from 2% to 10%. The FFC is assumed to have entered the particles via a surface process, and therefore the mass of FFC is weighted by the original surface area of the aerosol population. This method is appropriate if the FFC comes from the gas phase and is deposited on the surface as secondary aerosol mass. Other means of distributing FFC among particles are possible (e.g., weighted by particle mass), but here we explore only the surface weighting.

3. RESULTS

Results are presented by comparing the simulation output for two cases that are identical except that one assumes no FFC present, and the other adds some FFC. Unless otherwise stated, the total mass of FFC is 5% of the total aerosol mass. A given set of simulations comprises 2240 individual simulations for the range of aerosol size parameters and vertical velocities defined. Additional sets of simulations are derived by varying the amount, or distribution of FFC among particles. Each parcel model simulation proceeds until the cloud water content $\text{LWC}=0.5 \text{ g m}^{-3}$, and comparisons between sets of simulations are performed at this point.

Fig. 1 shows scatter plots of various parameters relative to their base case (no FFC) counterparts. It can be seen that the existence of FFC generally results in smaller r_{min} and in larger r_{max} , indicating that spectral broadening occurs toward both the smaller- and larger-drop ends of the spectrum. The result is that the relative dispersion D is almost always greater when FFCs are present, sometimes by more than an order of magnitude. The FFC tends to suppress drop number concentration $N_{d(s)}$, and maximum supersaturation S_s tends to be higher than S because growth is retarded and $N_{d(s)}$ is reduced. Note too the consistency between the suppression of $N_{d(s)}$ and the increase in $r_{e(s)}$. There are also many instances when the FFC does not modify these parameters, as indicated by the proliferation of points along the 1:1 line. There also exist a few points for which

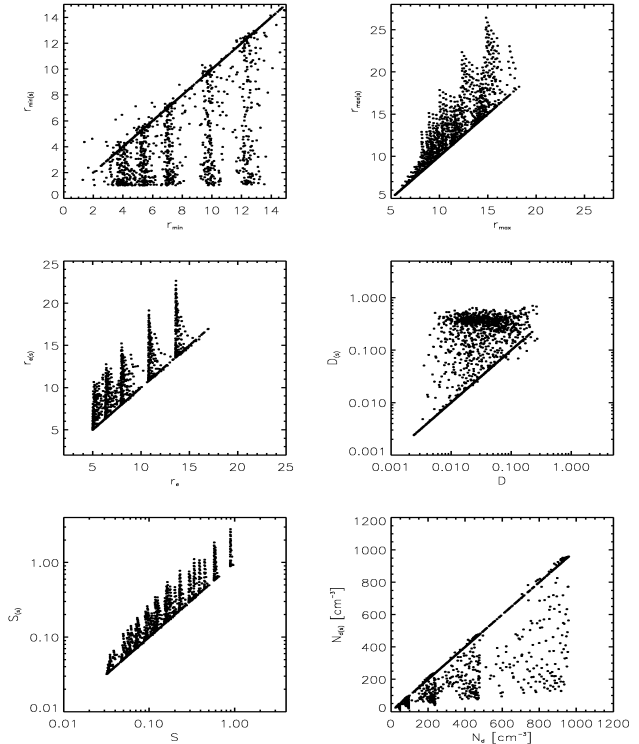


Figure 1: Comparisons between FFC modified simulations [subscript (*s*)], and standard parcel model simulations at the end of the simulation ($\text{LWC}=0.5 \text{ g m}^{-3}$). r_{min} is the minimum droplet radius $> 1 \mu\text{m}$; r_{max} is the maximum droplet radius for which drop number concentration is $> 1 \times 10^{-3} \text{ cm}^{-3}$; r_e is the effective radius; D is the relative dispersion of the drop spectrum, S is peak supersaturation; and N_d is total droplet concentration for $r_{min} \leq r \leq r_{max}$. FFC contributes 5% to the total aerosol mass and is weighted by surface area. The accommodation coefficient α experiences a jump from $\alpha=1 \times 10^{-5}$ to 0.042 when the monolayer ceases to exist.

dispersion is reduced by FFCs, but these occurrences lie below the 10th percentile (Fig. 2).

Droplet spectra for individual simulations for which $N_d=250 \text{ cm}^{-3}$, $r_g=0.08 \mu\text{m}$, $\sigma=1.7$, and $w=200 \text{ cm s}^{-1}$ are shown in Fig. 2 at the end of the simulation (112 s). These are conditions under which enhancement in D has been calculated. Spectra have been created from the discrete point model output by sampling to the size grid of a Forward Scattering Spectrometer Probe (FSSP). The distribution with FFC exhibits a relatively flat section below the modal radius which is qualitatively similar to some observations (e.g., Noonkester 1984 - Figs. 4 and 6; Gerber 1996, Fig. 7). It is significantly broader than the case in which particles are unaffected by FFCs. Figs. 2b and 2c reproduce some measured spectra from Noonkester (1984) and Gerber (1996) and indicate

qualitative similarity with the FFC-affected spectrum in Fig. 2a. Note that the observed spectra derive from a variety of locations, and are characterized by different LWC so that comparison is only qualitative.

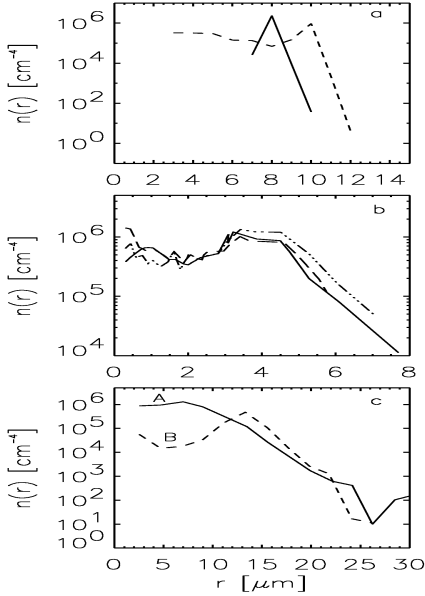


Figure 2: (a) Comparison between simulated drop spectra for FFC-free conditions (solid line) and including FFC (dashed line). Both spectra have a $LWC=0.5 \text{ g m}^{-3}$. (b) Cloud droplet spectra after Noonkester (1984) measured with an ASSP-100 (size range $0.23 \mu\text{m} \leq r \leq 14.7 \mu\text{m}$) about 35 m above the base of marine stratus clouds. (c) Cloud drop spectra after Gerber (1996) measured with an FSSP during ASTEX, 1992. The spectrum marked A is from a polluted air mass, and the one marked B is from a relatively clean marine air mass.

Figs. 3 and 4 examine more closely the evolution of the drop spectra to their final forms as depicted in Fig. 2a. Without FFCs (Fig. 3), whether particles are to become drops is determined during some small window of time, and thereafter drops grow in unison with concomitant narrowing of the spectrum. However, with FFCs, Fig. 4 indicates that in the early stages of cloud formation, a significant subpopulation of particles (i.e., those near the surface area modal radius) are unable to grow because of their film coatings. This allows both smaller and larger particles to grow much more rapidly than they would if these particles had been competing for vapor. Smaller particles overtake those whose growth is hindered and join larger particles to form the initial drop spectrum. As time progresses, FFC-laden particles are able to take up some water until their monolayers break; at this point they grow rapidly toward the existing droplet spectrum. Together they form the drop spectrum (Fig. 2a) that exhibits a characteristic flat tail comprising particles

that are relative newcomers to the droplet population and the modal radius that comprises drops that grew earlier in the process.

A sampling of numerous other individual spectra shows that this is the primary reason for spectral broadening for the conditions studied here. It raises the intriguing possibility that if FFCs do indeed act in this manner, there is not necessarily a 1:1 correspondence between aerosol size and drop size (see also Podzimek and Saad 1975).

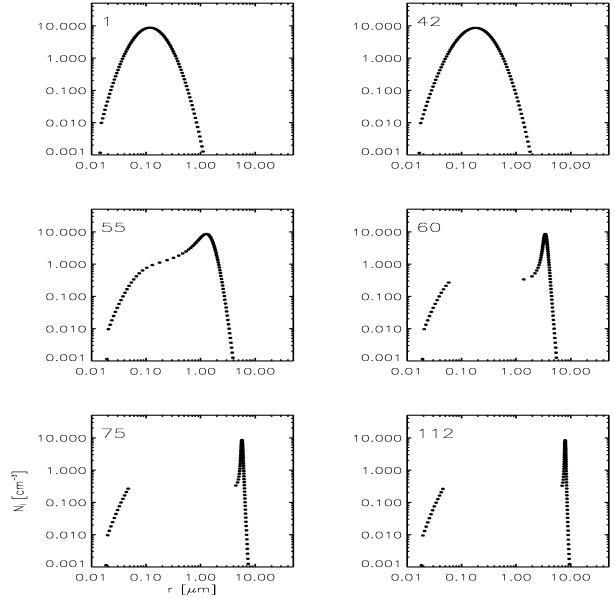


Figure 3: Droplet growth as a function of time (in seconds, indicated at upper left) for the FFC-free case. Points pertain to the raw model output of drop concentration in size category i (denoted N_i). Note the rapidly narrowing drop spectrum after 60 s.

Fig. 5 shows time series of various parameters for the base case and FFC simulations corresponding to Figs. 3 and 4. From early on in the simulation, D_s maintains a large value, but exhibits periodic oscillations. This is due to the discrete nature of the model representation of the aerosol spectrum. It reflects the fact that as individual size categories are freed of their monolayers and grow toward the drop spectrum, they enhance D_s . Until the next size category of particles experiences a break in its monolayer, the spectrum tends to narrow. These oscillations are therefore well correlated with oscillations in $r_{min(s)}$. In addition to significant enhancement in D_s , this case also exhibits a strong suppression in $N_{d(s)}$ during the early stages of spectral evolution. However, $N_{d(s)}$ increases steadily, and equals that of N_d at the end of the simulation. The lower $N_{d(s)}$ initially allows $S(s)$ to build up, but as with N_d , the differences between S and $S(s)$ are negligible by the end of the simulation. The enhanced r_{max} and r_e and suppressed r_{min} that were evident in Fig. 1 are shown to be a

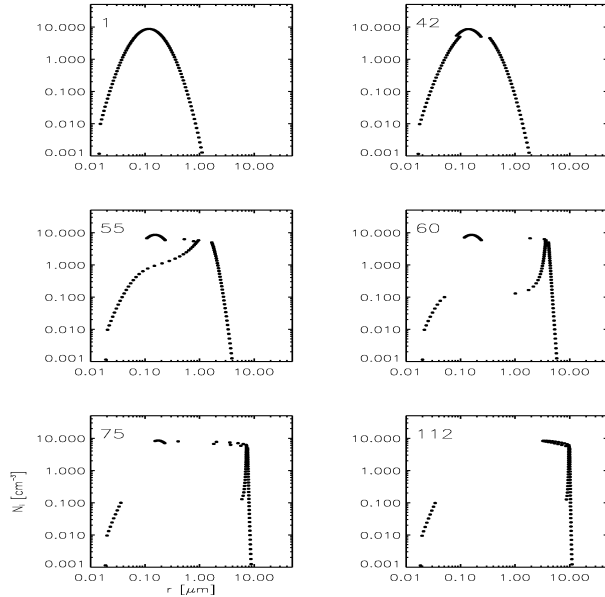


Figure 4: As in Fig. 3, but for particles with FFC. FFC retards growth of a large number of drops and enables the smaller and larger drops to grow and create the initial drop spectrum (at about 60 s). Later, FFC-laden drops near the aerosol mode break their monolayers and grow to join the initial drop spectrum (75 s – 112 s).

consistent feature for the duration of the simulation.

4. DISCUSSION

When the FFC material is concentrated near the surface modal radius, a significant percentage of particles is prevented from growing into droplets during the early stages of cloud formation. The result is that the largest particles combine with the smallest activated particles to form the initial drop spectrum. Only later, when monolayers break down, do the midsize particles join the spectrum. In doing so they create a rather broad, flat spectrum below the spectral mode that is sometimes observed in FSSP measurements. If FFCs are prevalent, and if our simulations mimic their behavior somewhat realistically, one may not need to look to other theories such as entrainment mixing to explain the observed enhancement in breadth – particularly in adiabatic cores of clouds that are unaffected by mixing. This is clearly not proof that the observed spectrum flatness is related to the presence of FFCs, but it is not inconsistent.

Suppression in N_d is significant when the FFC is weighted by spectral surface area. The suppression in N_d derives from the retarded growth of a significant fraction of the particle population, as well as to the evolution of the supersaturation field. Although many of the particles near the surface-modal radius eventually do grow to droplet sizes once their monolayers have broken, this occurs at a stage when the supersaturation

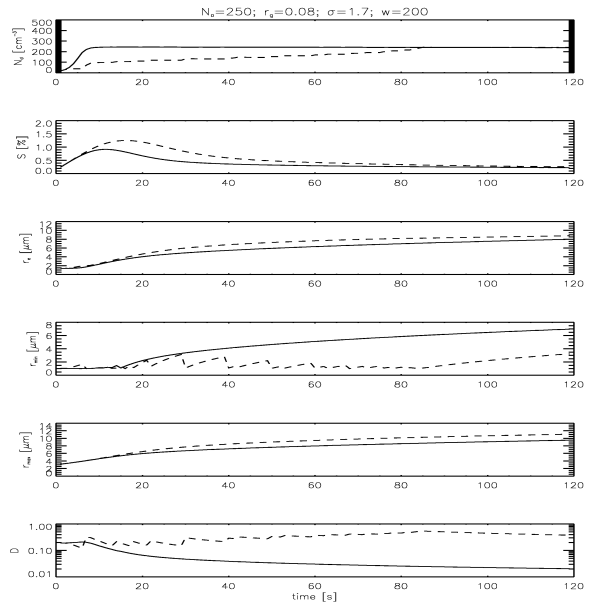


Figure 5: Temporal evolution of various parameters for the simulations described in Figs. 3 and 4. Solid lines are for the FFC-free simulation; dashed lines are for the simulation with FFC and the conditions described in Fig. 1.

is rapidly decreasing, with the result that some of them never attain droplet sizes.

Fig. 6 shows drop concentration vs. N_a for various combinations of modified condensation coefficient α , as well as % mass of FFC for the surface area-weighted distribution of FFC. Suppression of drop concentration increases with increasing FFC amount, as well as with decreasing α . For example, a 5% FFC mass contribution combined with a modified $\alpha = 10^{-5}$ yields a similar suppression to the case when the FFC mass contribution is 2%, but $\alpha = 10^{-6}$. When the modified $\alpha = 10^{-4}$, and the FFC mass contribution is 5% (line not shown) the power-law fit shows no change in the slope of the line compared to the case with no FFC. In this case, a significantly higher mass of FFC (>10%) is required to produce a noticeable suppression in drop number.

The reduction in N_d due to the existence of organic FFCs simulated here is opposite in trend to results that simulate the reduction in droplet surface tension due to the presence of organics (Facchini et al. 1999), and enhancement in N_d . We have not attempted to evaluate the relative importance of these processes. Whether organics ultimately enhance or reduce N_d is possibly case-dependent and worthy of further investigation.

To the extent to which our results represent natural cloud processes, they may represent an important factor in the aerosol-cloud-climate problem. Enhancement in drop dispersion aids the formation of larger drops that initiate collision-coalescence and precipitation. The depletion of cloud water by precipitation has

consequences for cloud radiative effects that are so much a part of the climate system. The feedback of precipitation to atmospheric dynamics is also important. In nonprecipitating clouds, a suppression of cloud droplet number would result in less reflective clouds (for an equivalent liquid water content), and this too could have climatic consequences. As an example, simulations in Figs. 3,4 yield visible cloud optical depths of about 13 for the case without FFC, and 11 with FFC – i.e., a reduction of 15%. Calculations of cloud reflectance using a simple two-stream approximation yield a reduction in cloud reflectance of about 10%.

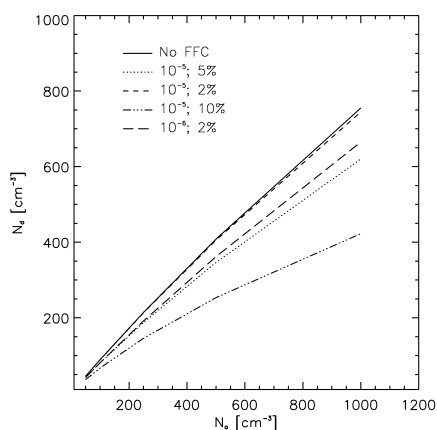


Figure 6: Drop number concentration N_d as a function of aerosol concentration N_a for a range of α and % contribution of FFC to total aerosol mass. FFC is weighted by surface area.

ACKNOWLEDGMENTS

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