

# Mechanisms of soot-aggregate restructuring and compaction

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## 1. Summary

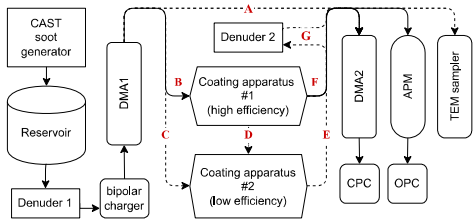
- Soot aggregates form as open-structured aggregates of spherical monomers.
- These aggregates are observed to restructure to more compact forms after the condensation and removal of liquid "coatings", which would result in more light absorption and more climate warming by soot black carbon.
- There has been ongoing debate about whether this compaction occurs during condensation or evaporation.
- Here, we present the results of a review of the surface science, where we identified experimentally constrained restructuring mechanisms. We also reviewed the soot-restructuring literature and identified unambiguous evidence of these mechanisms acting for soot particles (not shown here). Finally, we performed experiments designed to demonstrate the identified mechanisms.

## 2. Atmospheric implications

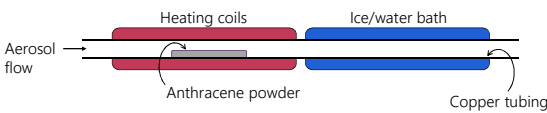
- Our work shows that soot particles mixed with condensing vapours in the atmosphere will *generally become compacted*. These condensing vapours may represent semivolatiles co-emitted with soot (e.g. lube oil from combustion engines) or formed via atmospheric oxidation (e.g. nitrates from ammonia use in agriculture).
- Compaction can be *avoided* when soot particles coagulate (collide with) other atmospheric particles. It is also feasible that solid coatings form in the atmosphere, when glassy semivolatile organics form at low humidity and temperature. These two routes may form soot which is "coated" but which does not display an enhanced climate warming potential, consistent with field observations.
- Future work will explore how the mechanistic insights provided in this work can be used to better constrain climate models.

## 3. Methods

- In the experimental study, we generated and selected 300 nm (mobility diameter) soot particles for coating addition and removal. We measured the mass of these particles before and after coating to determine the coating volume.

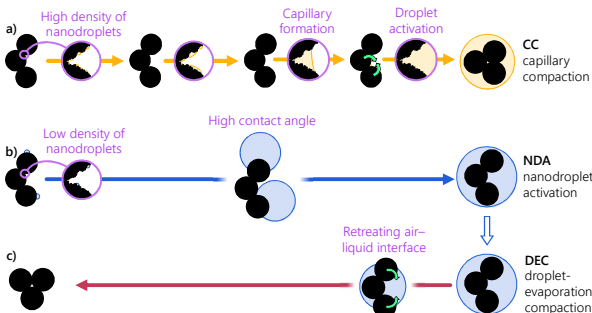


- We used two different coating apparatuses to vary the temperature and saturation ratio at which coatings formed. Thus, we were able to explore the phase diagram of anthracene to add and remove liquid or solid coatings to soot.



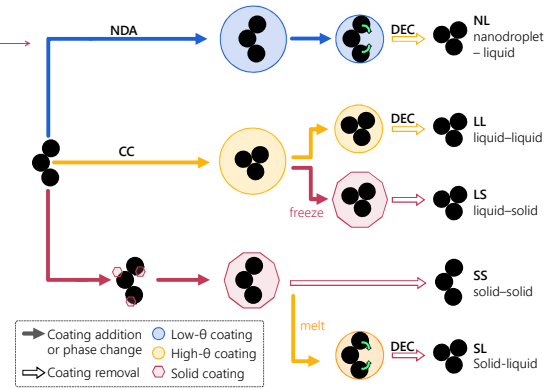
## 4. Soot restructuring mechanisms

Critically, we reviewed experimental evidence in the surface science literature to identify four significant mechanisms for soot restructuring. These occur when capillary forces are either generated or avoided at **critical stages of liquid-phase formation**. We reviewed 66 studies of soot restructuring and identified clear evidence for all illustrated mechanisms.



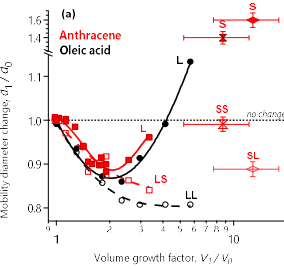
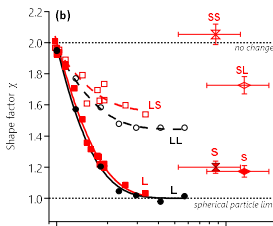
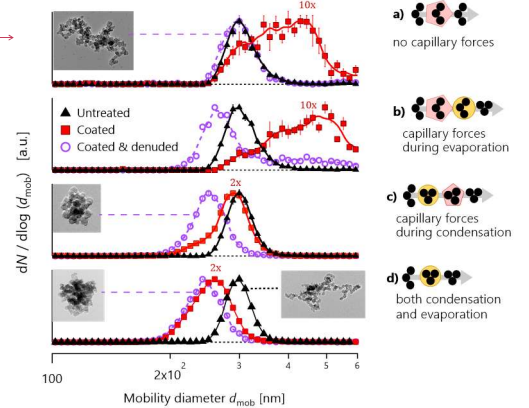
## 5. Experimental design

Using the phase diagram of anthracene, we designed experiments to isolate the effects of capillary forces to the processes of *condensation* (Path **LS**) or *evaporation* (Path **SL**), as verified by control experiments with no capillary forces (Path **SS**). Path **NL** requires a high liquid-soot contact angle, so could not be demonstrated with anthracene, but has been demonstrated in the literature with water. Path **LL** was additionally demonstrated with oleic acid for comparison with literature.



## 6. Experimental results

The panels to the right correspond to the experiments shown in Section 5. The control experiment (a) solid deposition and sublimation) and liquid experiments (b and c) together show that capillary forces result in restructuring, during both condensation and evaporation. The combination of both (b and c) in d, is further explored in Section 7.



## 7. Coating volume dependence

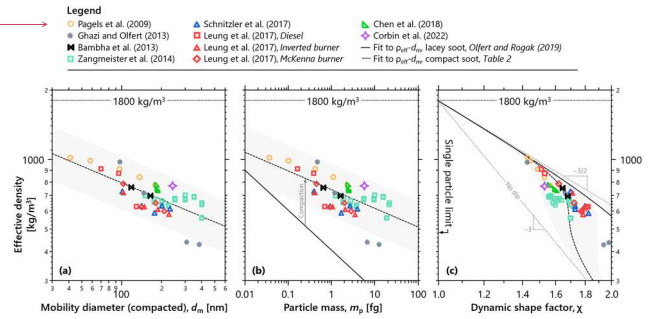
- The experiments in Section 5 were repeated at a variety of coating volumes.
- Liquid-coated soot became spherical (shape factor =1.0) when their volume was increased by a factor  $V_1/V_0$  of about 4.
- Denuded particles were more compact after **LS** than after **SL**, likely because the **SL** solid did not fully engulf the soot.
- Denuded particles were more compact after **LL** than after **LS**, likely because the condensation mechanisms act locally (where capillary forces arise) while the DEC mechanism acts on the entire aggregate.
- We performed fewer deposition experiments (**S**, **SS**, **SL**) than condensation experiments (**L**, **LL**, **LS**) due to practical limitations.

## 8. Universal compact soot relations

Combining these results with others in the literature allows us to define "universal" relations for restructured, compact soot. Using a similar approach to Olfert and Rogak (2019), we can define the following relationship:

$$\rho_{\text{eff}} = \rho_{\text{eff}100} \left( \frac{d_{\text{m}}}{d_{100}} \right)^{-\zeta}$$

where  $\rho_{\text{eff}100} = 794 \text{ kg/m}^3$  and  $\zeta = 2.76$ .



## 9. Conclusions and future work

- In addition to traditional *capillary* compaction mechanisms, a distinct mechanism for the mixing of soot with volatiles, *nanodroplet activation*, requires extreme supersaturations and was demonstrated in the laboratory. This mechanism explains previous, apparently conflicting experimental results.
- If condensation compaction is avoided, evaporation also leads to compaction.
- Our framework of condensation-compaction and evaporation-compaction mechanisms resolves conflicting conclusions in the literature and was demonstrated in the laboratory.
- The universal compact relations can be used to interpret particle mass analyzer measurements and to compute PM concentrations from SMPS data.