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Interactive comment on “Role of black carbon in the formation of primary organic aerosols: Insights from molecular dynamics simulations” *by* Xiaoqi Zhou et al.

Anonymous Referee #2

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This manuscript examines the estimated binding energies between a soot nanoparticle and volatile organic compound vapors compared with the self-binding energies among the organic vapors through a series of molecular dynamics simulations. While the simulations and energy estimation methods appear to be technically sound, the proposed relevance to atmospheric processes does not seem to be supported. The manuscript is thus recommended for rejection from ACP at this time.

General comments:

The main conclusion advocated by the authors is that VOC adsorption onto black carbon nanoparticles (NPs) plays an important role in formation of PM from VOCs because their binding energies to NPs are greater than their self-binding energies.

One confusing aspect of the manuscript is that the authors talk about aerosol nucleation, but the carbon NPs are already in aerosol form - so condensation of new material is not necessarily nucleating new particles. It could be argued that a new, condensed organic phase is being created/expanded via gas/particle partitioning (and thus contribute to initial condensation/"atmospheric aging") but the motivating discussion is not phrased this way.

The authors suggest that past correlations observed between BC and PM are due to the gas/particle partitioning mechanism they propose, but the correlation is more likely due to meteorology (varying boundary layer height) and transport (polluted air masses tend to contain both). And a large fraction of PM is inorganic, which is unexplained by the authors' hypothesis.

The binding energies the authors have compared are related to the adsorption energies and (free) activation energies for homomolecular nucleation. The atmospheric implications of the molecular dynamics calculations are better placed in context by incorporating their estimates into appropriate adsorptive gas/particle partitioning or nucleation models with atmospherically-relevant concentrations. However, it is generally regarded that homomolecular nucleation is not a likely mechanism for new particle formation in the atmosphere (based on past studies of binding energies and concentrations), so comparison of NP-binding energies to self-binding energies - particularly of VOCs - is not likely to yield a meaningful reference point on the significance of the former. The difference in binding energies though do support the layered mechanism of condensation observed in this work rather than organic island formation shown in many past molecular dynamics simulations of nanoparticles. (However, the universality of layered particles with soot at the center - i.e., core-shell morphology - has also been challenged by experimental data in the last decade.)

To determine the importance of the calculated NP-binding energies, the authors may refer to different adsorptive partitioning models - e.g., Pankow 1987 (reference below). On a mass basis, this mechanism (adsorptive partitioning) is generally considered to be less important overall than absorptive partitioning (also see articles by Pankow and co-workers on the topic). However, for certain toxic compounds, estimating the gas/particle partitioning behavior from computational simulations can prove useful and the authors may wish to direct their efforts in this area. (For analysis of experimental data for adsorptive/absorptive partitioning of aromatic and aliphatic organics, see also Pankow and co-workers' publications from the 90's.)

Pankow, J.F., 1987. Review and comparative analysis of the theories on partitioning between the gas and aerosol particulate phases in the atmosphere. Atmospheric Environment (1967) 21, 2275–2283. https://doi.org/10.1016/0004-6981(87)90363-5

Regarding the NP-binding energies, the simulation of a carbon NP is not entirely unreasonable since "fresh soot" is typically comprised of small, agglomerated spherules, albeit at varying sizes. However, the issue of sensitivity to surface curvature raised also by the other reviewer remains an impediment for interpreting the greater relevance of the current work. Extending the concept of the Tolman length to solids, there should be a size limit beyond which the curvature affects the results minimally, in the range where many carbon spherules and soot particles are found. Would not a comparison against binding to a flat graphene surface help alleviate this question?

Minor comments:

How large is the estimated binding energy compared to 1) variability among the local minima and 2) atomization energy of the BC itself?

Since an annealing process is used prior to the binding energy calculation, what temperature do these energies correspond to?

The word "catalytic" seems to be used colloquially but can be confusing in a chemistry-oriented paper.

The authors may wish to consider or discuss the conventional wisdom that soot is typically emitted with defects, surface functionalization, and coating by organic lubricants, etc. (I believe one of the authors of this manuscript has experience simulating adsorption on functionalized graphitic surface for this reason).

LAMMPS, as an acronym for Large-scale Atomic/Molecular Massively Parallel Simulator, is usually capitalized.

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Discussion paper