

Supporting Information: Multiscale Modeling of Human Skin Oil-Induced Indoor Air Chemistry: Combining Kinetic Models and Molecular Dynamics

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Updated Parameters

Table S1: All bulk diffusivities D_b , Henry’s law constants K , desorption lifetimes τ_d , and surface accommodation coefficients α_s updated through molecular dynamics simulations.

	$D_b/\text{cm}^2\text{s}^{-1}$	$K/\text{mol cm}^{-3}\text{atm}$	τ_d/ps	α_s
ozone	3.60×10^{-6} (*)	3.30×10^{-3} (*)	350	0.98
acetone	2.08×10^{-6}	5.44×10^{-4}	350	1.00
butanediol	1.81×10^{-6}	2.39×10^{-3}	710	1.00
4-OPA	1.56×10^{-6}	7.47×10^{-3}	1500	1.00
6-MHO	1.09×10^{-6}	8.29×10^{-2}		1.00
4-MOD	9.06×10^{-7}	2.68×10^{-1}		1.00
4-MON	7.62×10^{-7}	4.74×10^{-1}		1.00
GAC	5.88×10^{-7}	5.77		1.00

(*) previously reported in ref. 1

Free Energy Profiles

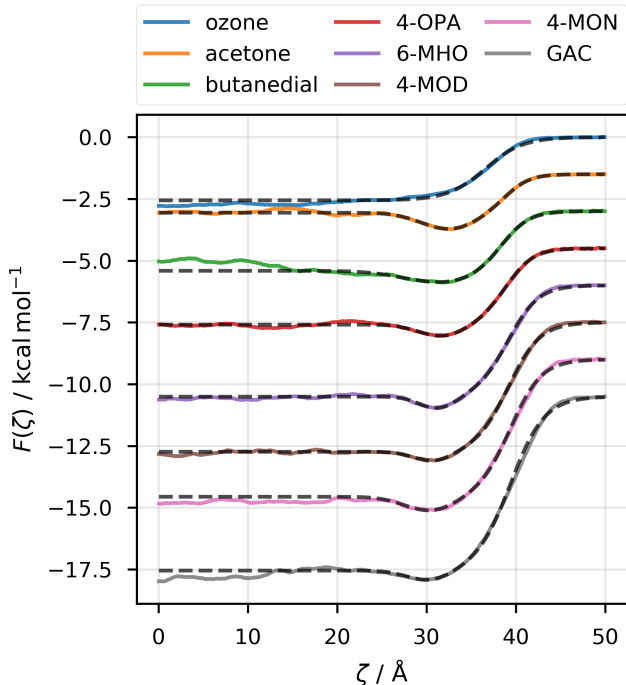


Figure S1: Solid lines: raw (but symmetrized) free energy profiles obtained from WTM-eABF calculations; with the exception of ozone, for which the data was taken from ref. 1. Dashed lines: the fitted empirical model functions, featuring a sigmoidal drop from the gas phase to the bulk and a Gaussian well describing the interfacial minimum for all molecules but ozone.

Outcomes of the Impinging Molecules Simulations

Table S2: Numbers of absorbed, adsorbed, desorbed, and scattered trajectories. Very rarely the initial velocity of a molecule is so slow that it does not reach the squalene slab within the time of our simulation. These cases were ignored, which is why some rows do not add up to 250.

	n_{abs}	n_{ads}	n_{des}	n_{scatt}
ozone	78	21	144	4
acetone	8	22	216	1
butanediol	20	102	125	0
4-OPA	58	109	79	0
6-MHO	93	138	16	0
4-MOD	94	145	4	1
4-MON	57	185	2	1
GAC	58	187	1	0

Interfacial Structure of Squalene

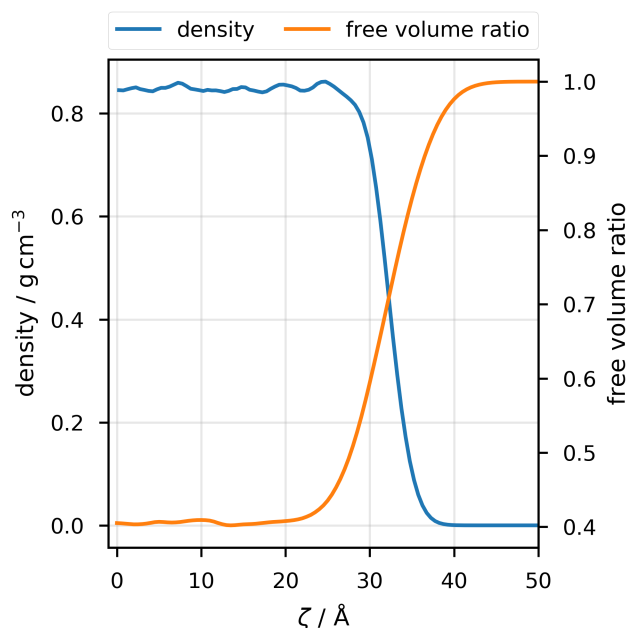


Figure S2: Total ζ -dependent mass density (blue curve, left axis) and free volume ratio (orange curve, right axis). The free volume ratio was calculated by dividing the simulation box in cubic cells of size $(0.5 \text{ \AA})^3$. Each cell that was within the van der Waals radius of any atom was marked as occupied; the other cells were marked as unoccupied. The free volume ratio is the number of unoccupied cells divided by the total number of cells.

Interfacial Free Energy Minimum

We have attempted to explain the presence/lack of an interfacial free energy minimum by studying the potential energy contribution $\Delta_{\text{solv}}U(\zeta)$ to the free energy profile of solvation $\Delta_{\text{solv}}F(\zeta)$, using ozone and acetone as representative solutes. We have furthermore split $\Delta_{\text{solv}}U(\zeta)$ into contributions from the intramolecular interactions within the slab, the intramolecular interactions within the solute, and the intermolecular interactions between solute and slab. The latter two are shown in Figure S3.

The profiles were obtained by recomputing and splitting up the potential energies of all configurations saved during the WTM-eABF simulations. The chosen trajectory output frequency was insufficient to accurately compute the intramolecular energy profile of the slab itself, for which the signal-to-noise ratio is very high, and thus this data is not shown here.

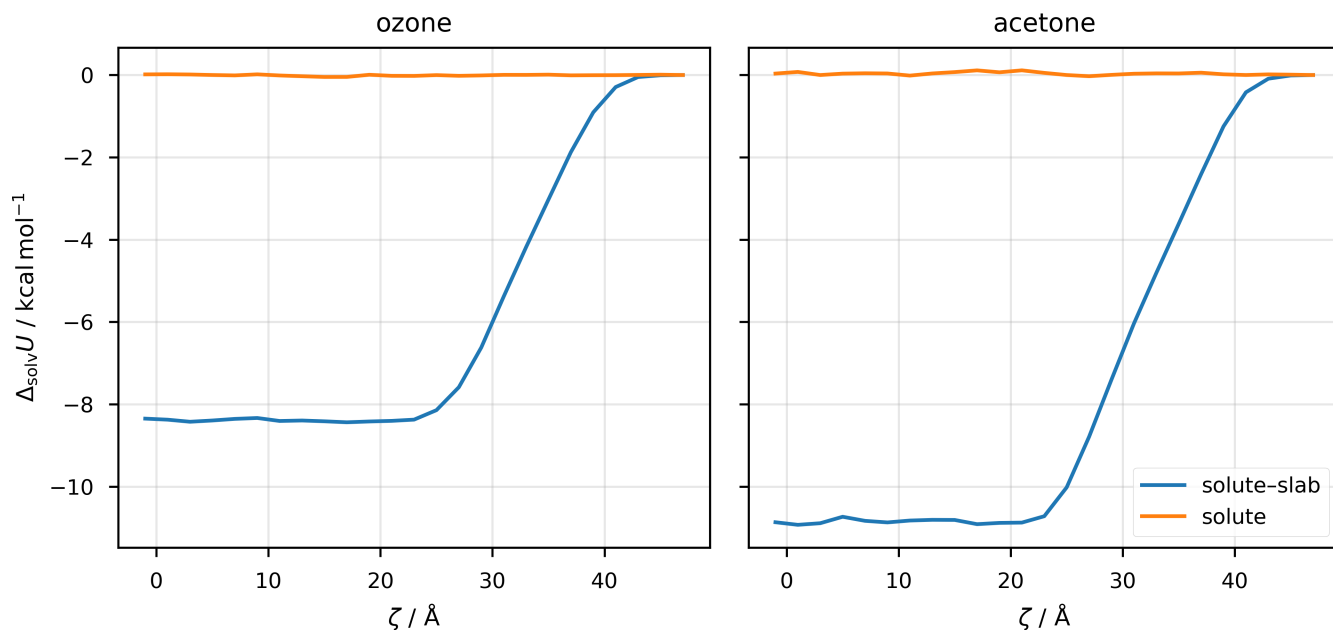


Figure S3: Potential free energy contribution $\Delta_{\text{solv}}U(\zeta)$ to the free energy profile of solvation for ozone and acetone. The lines correspond to the intramolecular interactions within the solute (orange) and to the intermolecular interactions between the solute and the slab (blue).

With the data at hand, we can confidently state that the free energy minimum in the

case of acetone is neither caused by enhanced interactions between the solute and the slab in the interfacial region of our system, nor by intramolecular rearrangements of the solute. The minimum must instead have entropic origins and/or could be caused by a stabilization of the interface when a solute is present, which would show up in the missing free energy profile. In both cases, an explanation for the differences between ozone and acetone could lie in simple size effects. Since the primary objective in this article was the determination of the free energy difference between the gas phase and the bulk-like phase, which is not affected by this discussion, we did not follow up on these ideas.

References

- (1) Lakey, P. S. J.; Morrison, G. C.; Won, Y.; Parry, K. M.; von Domaros, M.; Tobias, D. J.; Rim, D.; Shiraiwa, M. The Impact of Clothing on Ozone and Squalene Ozonolysis Products in Indoor Environments. *Commun. Chem.* **2019**, 2, 1–8.