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PARTI-SUITE TRAJECTORY CODES DESCRIPTIONS

TRAJ-HAP, TRAJ-JET, and TRAJ-PAR

Abstract

Describes:

- a) Input parameters
- b) output files for fluxes and trajectories
- c) time step and other transport parameters

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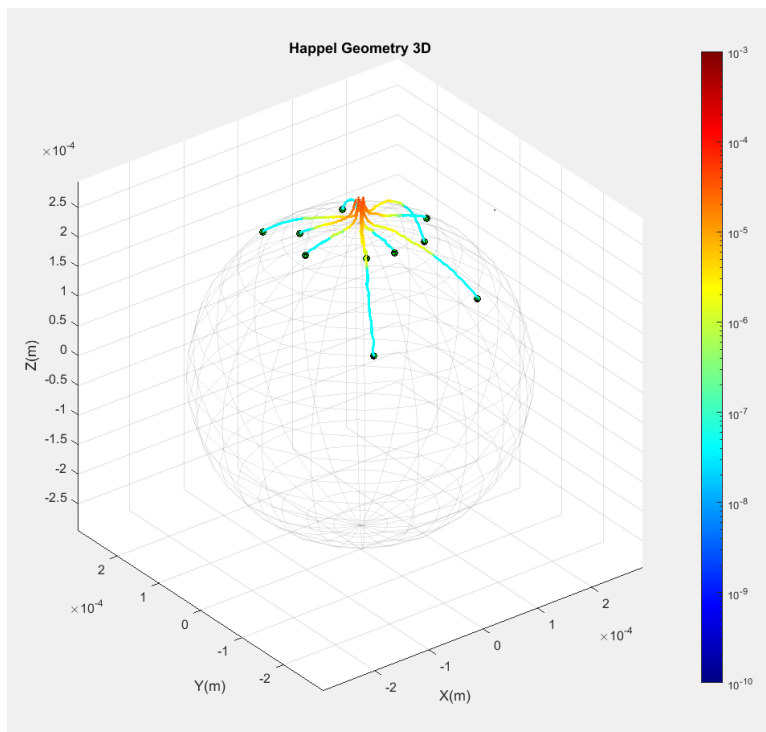
Summary

Mechanistic pore scale Lagrangian trajectory simulations using full force and torque balance on particles in the respective flow fields and collector geometries are provided in Traj-Hap (Happel sphere-in-cell), Traj-Jet (impinging jet) and Traj-Par (parallel plate). Detailed descriptions of the force and torque balance are provided in W.P. Johnson Research Group publications (<http://www.wpjohnsongroup.utah.edu/>; or https://scholar.google.com/citations?user=C9gB_GgAAAAJ&hl=en&authuser=1), see in particular Pazmino et al. (2014), Trauscht et al., (2014), Ron et al., (2019), Rasmuson et al., (2019), and VanNess et al. (2019), and references therein.

The pore-scale Lagrangian trajectory simulations were originally written in Fortran, from which the codes were parallelized to allow simulation of simultaneous trajectories, since any given trajectory may require upwards of hundreds of trillions of time steps. The software is herein provided as ported MatLab executables for clear visualization of trajectory simulations of colloid populations numbering in the tens to hundreds depending on simulation parameters (which define computational intensity). At a minimum the Matlab codes provide visualization and teaching opportunities. Once the user has understood the Matlab executables, we encourage use of the Fortran executables, which allow simulation of populations of hundreds to thousands (depending on simulation conditions). To facilitate parallelized simulation of larger particle populations (thousands to tens of thousands) we intend to provide Python-based easily parallelized software in the near future (hopefully early 2020), but we are also willing to collaborate on Fortran-based parallel simulations on our platform for interested users. For simulations not reasonably attainable via the Matlab or Fortran executables, please feel free to

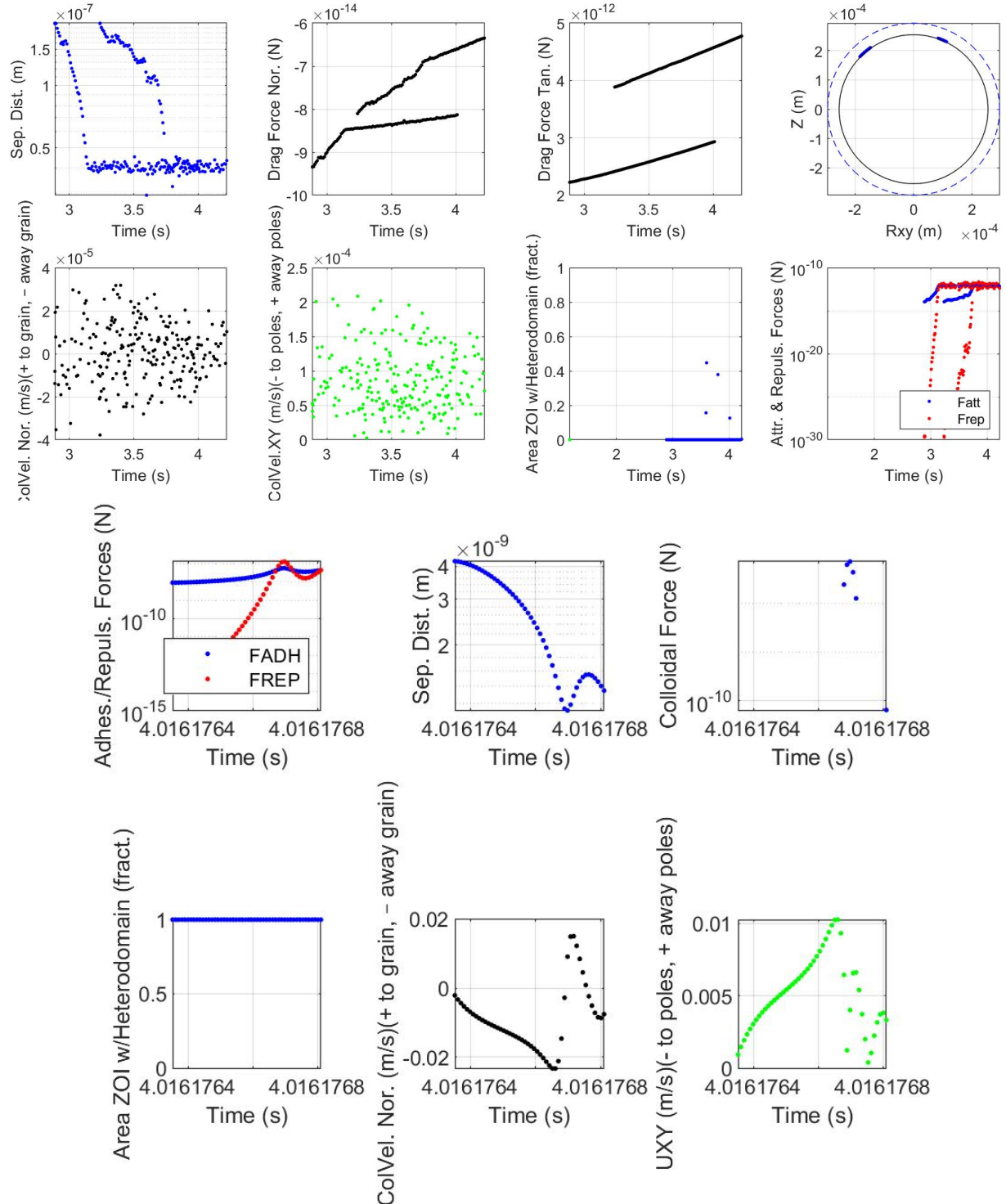
contact us with requests for parallelized simulations.

The codes can be run in “contact” versus “perfect sink” modes: Contact (where contact mechanics applies) is defined as separation distances within which the combined near surface forces (absolute values of steric, Lewis acid-base, and Born) exceed 0.01% of their values at equilibrium separation distance in vacuum (~ 0.0158 nm). Contact distances range from < 1 to several nm depending on steric and Lewis acid-base forces. Diffusion is not considered in the force and torque



balance when contact mechanics applies. In contrast to contact mode, perfect sink mode arrests the colloid once it achieves a separation distance defined as contact (defined in preceding paragraph).

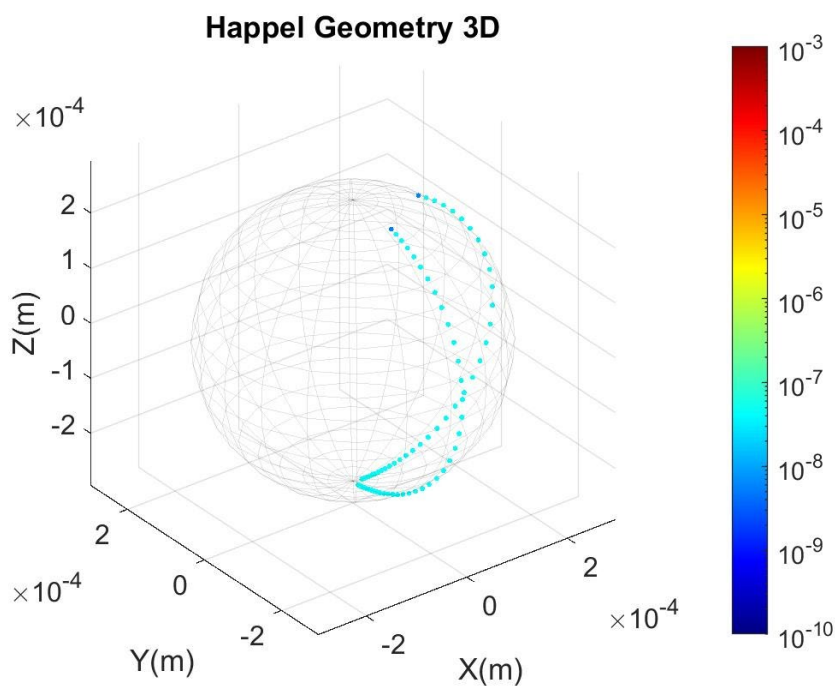
The code provides graphical progress during the simulation, as shown for Traj-Hap, below for two trajectories during transport in the near-surface (top) and contact (bottom):



The current versions of the trajectory codes place nanoscale heterogeneity on the collector rather than colloid surfaces, for reasons described in our publications. We anticipate distributing versions that allow placement of nanoscale heterogeneity on colloids (Summer 2019).

An important consideration is that colloids may attach at the rear flow stagnation point (RFSP). When heterogeneity is generated, the model generates a heterodomain at the RFSP in order to allow fast resolution of RFSP colloids as attached (ATTACHK=2). However, because all flowlines converge at the RFSP, the ZOI and heterodomain are guaranteed to completely overlap at the RFSP. Hence, RFSP colloids are not considered truly attached, but rather may expel to bulk fluid or to the near surface of a downgradient grain, as parameterized in UpscaleContinuum. For this reason, RFSP colloids should be subtracted from the attached population for the purpose of calculating collector efficiency, as also parameterized in UpscaleContinuum.

Detachment simulations can also be run in the trajectory codes by specifying perturbation mode in the GUI. The software will prompt the user for the trajectory flux attached and remaining files to be read in to the simulation. All parameters used in the trajectory simulations will be loaded from the flux attached file. However the user has the option to reset some parameters in the GUI to drive perturbation (e.g., by altered ionic strength, ζ -potential, fluid velocity, etc.). Note that the trajectory codes allow numerical efficiency to be improved by recognizing the practical arrest of very slow moving colloids in contact with the collector surface (using DFACTC and DFACTNS). This may produce functionally arrested colloids designated with ATTCHK=4 in the summary flux files for “remaining” colloids (HAPHETFLUXREM). The user may opt to include these colloids in the perturbation simulation



by toggling the corresponding GUI button when specifying the trajectory flux file to be read into the software.

Traj-Hap, Traj-Jet, and Traj-Par each produce ASCII files that can be further processed by users, and are typically more useful than the GUI outputs. These files are found in the

program directory with specific path differing with user environment. For example: C:\Program Files\W.P. Johnson Research Group\Jet_Trajectory_GUI0.11\application\JetWorkdir001, wherein the path above “W.P. Johnson Research Group” will differ with user environment.

ASCII files output by Traj-Hap, Traj-Jet, and Traj-Par include:

- a. Summary flux files for the population of particle trajectories, described in detail below.
- b. Selected trajectory files for individual particles, described in detail below.

We suggest that you initiate your simulations with larger colloids ($> 1 \mu\text{m}$) and higher fluid velocities ($> 10 \text{ m/day}$) and favorable conditions, that will allow rapid simulation for familiarization, and then lower these values as desired. As you decrease fluid velocities and colloid sizes, you will also want to increase the time step multipliers, within numerical limits. Note that time step multipliers should always be > 1 for the near surface and bulk fluid domains in order to preserve random motion representative of diffusion.

We would like to emphasize that the contact, steric, roughness and heterodomain parameters were developed over across a variety of conditions described in Ron et al., (2019), Rasmuson et al., (2019), and VanNess et al. (2019), and references therein. The current parameterization is fully substantiated in experimental observations. Conditions not currently addressed include: a) roughness of magnitude that generates new impinging surfaces in the flow field; b) dual porosity domain impacts on attachment; c) heterogeneity on colloids; d) non-spherical colloids. However, each of these unaddressed conditions are points of potential improvement, and we welcome suggestions and collaborative efforts to address them.

Information is provided below regarding: a) input parameters; b) output files, and c) input parameter detailed information for run-time and output parameters not described in supporting information of publications.

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Pazmino E., Jacob Trauscht, and Johnson W.P., 2014, Release of Colloids from Primary Minimum Contact Under Unfavorable Conditions by Perturbations in Ionic Strength and Flow Rate, *Environ. Sci. Technol.*, 48(16), 9227–9235, DOI: <http://dx.doi.org/10.1021/es502503y>.

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Trauscht J., E. Pazmino, and W.P. Johnson, 2015, Prediction of Nanoparticle and Colloid Attachment on Unfavorable Mineral Surfaces Using Representative Discrete Heterogeneity, Langmuir, 31 (34), 9366–9378, DOI: <http://dx.doi.org/10.1021/acs.langmuir.5b02369>.

VanNess Kurt, Anna Rasmuson, Cesar A. Ron, William P. Johnson, 2019, A Unified Theory for Colloid Transport: Predicting Attachment and Mobilization under Favorable and Unfavorable Conditions, Langmuir, 35 (27), 9061-9070, 10.1021/acs.langmuir.9b00911.

Trajectory codes (TRAJ-HAP, TRAJ-JET, TRAJ-PAR) input parameters

NPART: number of colloids simulated

ATTMODE: For perfect sink enter 0, for torque balance enter 1. Perfect sink mode considers the particle as attached when separation distance < 1 nm. Torque balance mode considers whether the resisting torque exceeds the driving torque (arrest) in contact (separation distances less than that of barrier maximum, *ca.* 1 nm).

VSUP (m/s): Fluid superficial velocity. For Traj-Hap = product of average pore water velocity (v) and volumetric water content (θ) ($VSUP = Q/A = \theta v$). For Traj-Jet = flow (Q) divided by cross sectional area (A) of jet ($VSUP = Q/A$).

RLIM (m): Injection radius. RLIM should be slightly larger than the radius over which colloids have zero probability of intercepting the surface, but should not be smaller than this radius. Otherwise the collector efficiency will be underrepresented. If RLIM is too large, most colloids will not approach the surface. The importance of RLIM will increase parallelization allows larger populations to run.

REXIT (m): The radius beyond which colloids exit the observation area of the impinging jet system

POROSITY (-): Porosity of porous media used to scale Happel fluid envelope. Equal to volumetric water content in these saturated systems.

AG (m): Happel Collector Radius

AP (m): Colloid radius

RHOP (kg/m³): Colloid density

RHOW (kg/m³): Fluid density

VISC (kg/m/s): Fluid viscosity

ER (-): Relative permittivity of fluid

T (K): Temperature in Kelvin

IS (mol/m³): Ionic strength of electrolyte in solution

ZI (-): Valence of electrolyte in solution

ZETAP (V): Colloid zeta potential

ZETACST (V): Collector zeta potential

ZETAHET (V): Heterodomain zeta potential

HETMODE: Sum of numbers of small and large heterodomains in each patch (HETMODE = 5 yields 1 large heterodomain surrounded by four equally spaced small heterodomains. HETMODE = 1 yields uniform sized heterodomains)

RHETO (m): Radius of large heterodomain

RHET1 (m): Radius of small heterodomains

SCOV (1): Fractional surface coverage occupied by heterodomains. To eliminate heterogeneity, set surface coverage by heterodomains to zero.

A132 (J): Combined Hamaker constant, applies only for VDWMODE = 1 (uncoated system)

LAMBDAVDW (m): vdW decay length

VDWMODE: 1 = non-layered surfaces, 2 = layered colloid and layered collector, 3 = non-layered colloid and layered collector, 4 = layered colloid and non-layered collector

A11 (J): Colloid Hamaker constants, set to 0 if VDWMODE=1

AC1C1 (J): Colloid coating Hamaker constant, set to 0 if VDWMODE=1

A22 (J): Collector Hamaker constant, set to 0 if VDWMODE=1

AC2C2(J): Collector coating Hamaker constant, set to 0 if VDWMODE=1

A33 (J): Fluid Hamaker constant, set to 0 if VDWMODE=1

T1 (m): Colloid coating thickness, set to 0 if VDWMODE=1

T2 (m): Collector coating thickness, set to 0 if VDWMODE=1

GAMMA0AB (J/m²): Acid base energy at minimum separation distance

LAMBDAAB (m): Acid base decay length

GAMMA0STE (J/m²): Steric energy per unit area at zero separation distance

LAMBDASTE (m): Steric decay length

B (m): Slip length for hydrodynamic influence of roughness (typically equal to maximum roughness asperity height)

RMODE (-): Set to 0 for no roughness (RMS roughness < 5 nm), 1 for rough colloid, 2 for rough collector, and 3 for rough colloid & collector.

ASP (m): Asperity height used to calculate DLVO interactions. Value is between 5-20 nm, as smaller asperities are superimposed on larger asperities, and in our experience is equal to RMS roughness on colloid.

ASP2 (m): Maximum asperity height on surface used to calculate enhanced arresting torque lever arm when multiple points of contact are possible (i.e., spacing between maximum asperities can accommodate colloid, generally true if colloid:asperity ratio is < 10).

KINT (N/m²): Combined elastic modulus of colloid and collector

W132 (J/m²): Work of adhesion

BETA (-): Expected fraction of maximum colloid-collector contact radius prior to arrest. Set to 1.0 for detachment, <1.0 (but > 0) for attachment

DIFFSCALE (-): Diffusion scaling factor to reconcile diffusion force to Stokes-Einstein displacement. Set to 1.35

GRAVFACT (-): Set to -1.0 for flow concurrent to gravity, 1.0 for flow countercurrent to gravity, 0.0 for no gravity

MULTB (-): Time step multiplier applied to momentum relaxation time when colloid is in bulk fluid

MULTNS (-): Time step multiplier applied to momentum relaxation time when colloid is in near surface

MULTC (-): Time step multiplier applied to momentum relaxation time when colloid is in near surface

DFACTNS (-): Near-surface displacement factor = the multiple of predicted Brownian displacement for the average of a population below which the program will consider the colloid retained without attachment. Because displacement for a given colloid at a given time is being compared to an average displacement in a population, DFACTNS needs to be $\ll 1$ to avoid premature flagging of particles as retained without attachment. We typically use $DFACTNS = 1.0E-5$ to discriminate slow-moving near-surface colloids in order to avoid excessive computation time.

DFACTC (-): Contact displacement factor = the multiple of predicted Brownian displacement for the average of a population below which the program will consider the colloid arrested. Because displacement for a given colloid at a given time is being compared to an average displacement in a population, DFACTC needs to be < 1 to avoid premature flagging of particles as retained without attachment. We typically use $DFACTC = 1.0E-1$ to discriminate slow-moving in-contact colloids in order to avoid excessive computation time.

NOUT: Output interval for trajectory files. Decreasing NOUT will increase trajectory resolution but will increase file size.

PRINTMAX: Maximum output array size for trajectory files. Typically set to 10,000

Description of Summary flux files for the population of particle trajectories from TRAJ-HAP, TRAJ-JET, or TRAJ-PAR

Flux files output from both Traj-Hap and Traj-Jet are titled as HAPHETFLUX***, where *** is replaced by ATT, REM, or EX for particles that were attached, functionally attached or retained without attachment, or exited.

Flux files provide (for the particle population) the following parameters:

PARTICLE # (injection order)

HINIT(m), XINIT(m), YINIT(m), ZINIT(m), RINJ(m) (initial separation distance from surface, as well as x,y,z and radial locations of colloid center in injection plane)

HOUT(m), XOUT(m), YOUT(m), ZOUT(m) (final separation distance from surface, x, y, and z locations)

PTIMEIN(s), PTIMEOUT(s) (time of injection, time of exit, attach or identified as remaining)

ETIME(s), TBULK(s), TNEAR(s), TFRIC(s) (elapsed time in collector prior to exit, attach, or identified as remaining, elapsed time in bulk fluid, elapsed time in near surface fluid, elapsed time in contact)

NSVISIT (number of visits to near surface fluid), FRICVISIT (number of visits to contact)

ATTACHK (number corresponding to retention mode: 1=EXIT ATTACHK2=ATTACHED-BY-PERFECT-SINK-OR-TORQUE, ATTACHK3=REMAINING-IN-BULK-FLUID, ATTACHK4=TORQUE-WITH-SLOW-MOTION, ATTACHK5=IN-NEAR-SURFACE-WITH-SLOW-MOTION, ATTACHK6=CRASHED)

AFRACT (area if colloid-surface ZOI occupied by heterodomain)

HETTYPE (number corresponding to size of heterodomain)

NSVEL(ms-1) (near surface colloid velocity, determined from < 200 nm residence periods)

HAVE(m) (average separation distance in near-surface)

The different colloid outcomes designated by ATTCHK are further described as follows: ATTCHK1=EXIT (exited colloids), ATTCHK2=ATTACHED-BY-PERFECT-SINK-OR-TORQUE (arrested fully), ATTCHK3=REMAINING-UNRESOLVED-WHEN-SIMULATION-ENDS (remained in bulk fluid or near surface when simulation ended), ATTCHK4=TORQUE-WITH-SLOW-MOTION (designated as attached using DFACTNS), ATTCHK5=IN-NEAR-SURFACE-WITH-SLOW-MOTION (designated as attached using DFACTNS), ATTCHK6=CRASHED (negative colloid:surface separation distance obtained, avoid these by reducing time step MULT parameters for near surface and contact). More information regarding DFACTNS and DFACTC are provided below.

Description of Output Trajectory files for individual particle trajectories from TRAJ-HAP, TRAJ-JET, or TRAJ-PAR

Trajectory files output from both Traj-Hap and Traj-Jet are titled as HAPHETTRAJ***, where *** is replaced by ATT, REM, or EX for particles that were attached, retained without attachment, or exited. Trajectory files provide (for individual colloids) the following parameters:

X, Y, Z, I, H (x,y,z location of colloid center, number of time steps, colloid-surface separation distance)

FCOLL, FEDL, FVDW, FDRGX, FDRGY, FDRGZ, FDIFX, FDIFY, FDIFZ (forces for total colloid-surface interaction, electric double layer, van der Waals, fluid drag x,y,z components, diffusion force x,y,z components)

UX, UY, UZ (colloid velocity x,y,z components)

VX, VY, VZ (fluid velocity x,y,z components)

PTIMEF (time of simulation)

AFRACT (fraction of colloid-surface ZOI occupied by heterodomain)

Run-time and output parameters in TRAJ-HAP, TRAJ-JET, and TRAJ-PAR trajectory simulations

Guidance regarding DRNH (RHET and SCOV) and provided immediately below. Further below we provide information regarding run time parameters (RLIM, DFACT, MULT) that is not provided in Supporting Information in our publications:

- RHET and SCOV

- *Rationale*

Discrete representative nanoscale heterogeneity (DRNH) is assumed by our code to follow a Pareto type distribution wherein the number-based frequency of heterodomains (nanoscale attractive zones) increases geometrically with decreased heterodomain size, reflective of a clustering phenomenon.

- *Method*

The spreadsheet “SCOV calculator” is provided on the distribution site. On the worksheet, the user specifies the grain radius, as well as the colloid diameters. From this information, the spreadsheet determines the appropriate heterodomain sizes capable of arresting and releasing each colloid size based on carboxylate-modified polystyrene latex microspheres on silica (Ron et al., 2019; VanNess et al., 2019; Rasmuson et al., 2019). The relationship may apply to other colloids and surfaces; however, its broader applicability is currently undetermined. The spreadsheet calculates surface density, # of heterodomains, and surface coverage (SCOV) wherein the latter is used by the trajectory code for the given heterodomain size. Please note that whereas the code can utilize multiple heterodomain sizes, we recommend utilizing a single heterodomain size (HETMODE = 1, with only RHET0 defined) for each simulation.

- RLIM (Injection Radius)

- *Rationale*

Beyond a specified limiting radius, the particle trajectories have zero chance of intercepting the surface. To save computational time, the particles may be injected over a radius (RLIM) specified in the input file. RLIM should be slightly larger than the radius over which the particles have zero probability of intercepting the surface but should not be smaller than this radius.

- *Sensitivity*

RLIM is a function of particle size, collector size, and fluid velocity. For example, small particles experience enhanced diffusion which will allow them to cross streamlines and intercept the surface.

- *How to test*

Always test RLIM under favorable conditions (opposite zeta potentials for collector and particle surface and SCOV set to 0.0) under SEP mode (ATTMODE = 0). It is instructive to plot the XINIT and YINIT locations of the exited and attached populations to visualize the limiting radius (Figure 3).

Another method to determine if a sufficient RLIM has been selected is to plot eta versus RLIM under favorable conditions. Eta should form a plateau beyond a specific RLIM value, and then

dramatically decrease below this value (Figure 4). A representative RLIM should be selected along the plateau.

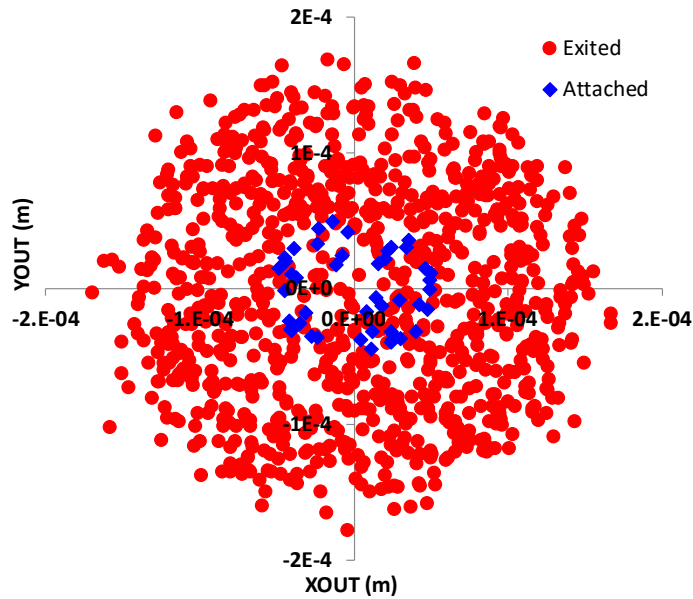


Figure 3: Final attached (blue diamonds) and exited (red circles) locations.

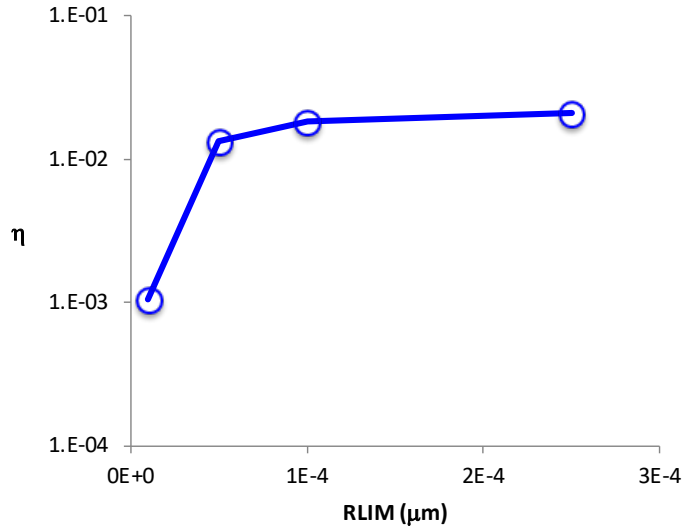


Figure 4: Collector efficiency (η) as a function of RLIM.

- DFACTC (Contact displacement factor) and DFACTNS (Near surface displacement factor) both input under Slow motion parameters
 - *Rationale*
 - This allows slow-moving particles in the near-surface and friction mode to be flagged in order to avoid excessive computation time.

- It is important to note that **only ATTACHK=2 is considered true attachment**. Particles flagged as ATTACCHK 3 are remaining in fluid when simulation ends, and are therefore unresolved. Particles flagged as ATTACHK 5 are flagged as moving very slow in the near surface fluid and their simulation is terminated according to the user-input DFACTNS. Particles flagged as ATTACHK4 are flagged as moving very slow in contact, and their simulation is terminated according to the user-input DFACTC.
 - If DFACT is too large, the particles may be flagged before they reach their final equilibrium colloid-surface separation distance (Figure 1).
 - If DFACT is too small, the particles will take a long time to be flagged, increasing computation time.
 - *Method*
 - DFACTNS and DFACTC are used to determine if the particle displacement measured over a specified number of timesteps is less than a factor (DFACT) of the expected displacement due to diffusion.
 - This test is applied when the particle is in the near surface (H is less than 200 nm) and when the particle is in contact (H is less than HFRIC) with DFACTNS and DFACTC applying to the respective separation distances.
 - If the condition is satisfied in the near surface, the particle is flagged as remaining (ATTACHK=5), and if the condition is satisfied in contact, the particle is flagged as remaining in contact (ATTACHK=4).
 - *Sensitivity*
 - Before using the model, a sensitivity analysis such as the one presented below should be conducted to constrain DFACT1 and DFACT2. As a general rule of thumb, we advise setting both DFACT values to a low number (i.e. < 0.1) to avoid flagging particles as remaining and increasing DFACT only if the model is running slowly.
 - DFACT values are $\ll 1$ because the actual net translation at the surface (or near surface) after 1000 time steps is compared to the translation expected from diffusion in bulk solution (Stokes-Einstein). Because hydrodynamic retardation greatly reduces the translation at (or near) the surface relative to bulk (unbounded) solution, the net translations may be (are typically) very small relative average Stokes-Einstein translation in bulk solution.
 - For 2.0 μm colloids under unfavorable conditions, DFACTNS and DFACTC were calibrated to 0.001, and 0.1, respectively.
 - Increasing DFACT above the calibrated values will flag particles as remaining (Figure 2), whereas values decreasing DFACT below the calibrated values yields no flagged particles.

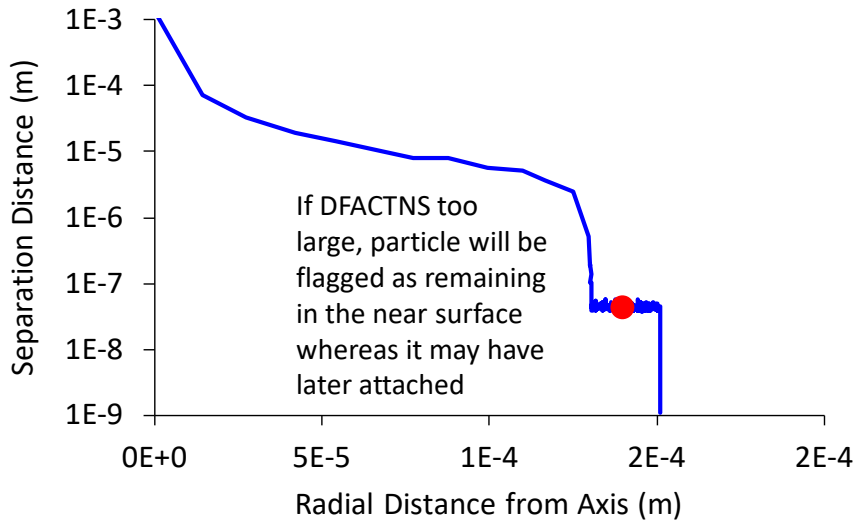


Figure 1: Particle trajectory showing flagged particle (red circle) in near surface as a result of DFACTNS being too high.

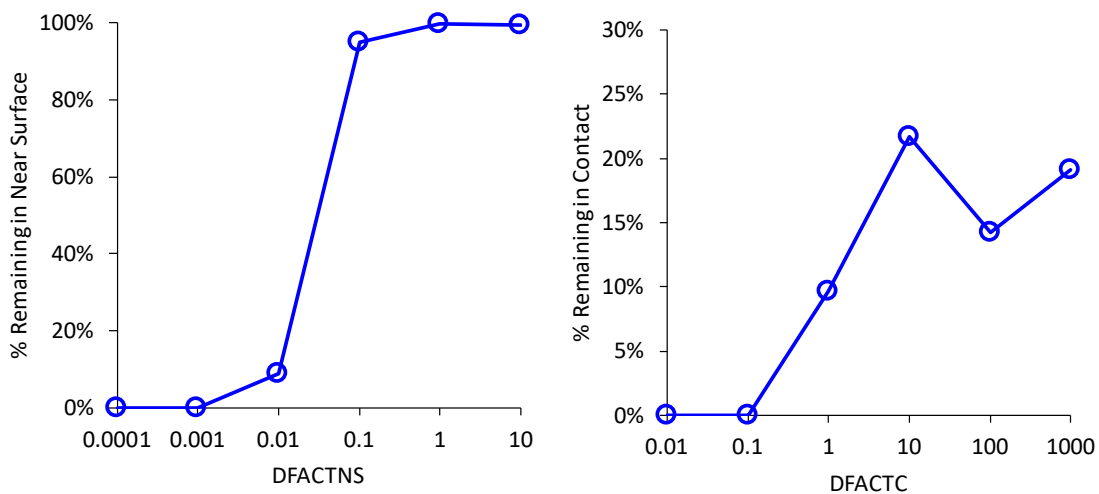


Figure 2: Percentage of particles remaining in near surface (left panel) and contact (right panel) as a function of DFACT.

- MULT (Time step parameters)
 - *Rationale*
 - Below a certain timescale diffusion-related particle motion is correlated. It is only above a certain timescale that the diffusion randomness emerges. If you impose this behavior in a regime that is close to the moment relaxation time you will impose randomness when the motion is indeed correlated.
 - *Method*
 - The timestep is set by $dt = \text{MULT} * dt_{\text{MRT}}$ (particle moment relaxation time).
 - Three different MULTS are used according the separation distance:

- MULT = bulk fluid ($H > 2.0E-7m$)
- MULT2 = near surface domain ($H_{FRIC} > H > 2.0E-7m$)
- MULT3 = contact domain ($H < H_{FRIC}$)

where H_{FRIC} is the separation distance where contact is considered to occur).

- Note that in contact mode diffusion is turned off. Therefore, MULT3 can be a small number (i.e. less than 1) without violating diffusion.
- *Sensitivity*
 - If MULT or MULT2 are too large the particle displacement in a single timestep may become large enough to skip over the contact domain and “crash” the particle into the surface (i.e. $H < 0$). This is flagged by ATTACHK=6 in the attached flux file.
 - If ATTACHK=6 occurs, the user can decrease MULT and MULT2 in order to avoid crashing the particle.
- NOUT
 - Sets the interval to output to the trajectory file.
 - If NOUT is too large, the resolution of the trajectory file may be too coarse.
 - If NOUT is too small, PRINTMAX will be exceeded (see below) and detailed information will only be stored for the end of the trajectory.
- PRINTMAX (Maximum output array length)
 - Sets the maximum number of lines to print to the output array.
 - If printmax exceeded, the array will be overwritten starting at the second line (i.e. the first line of the previous trajectory file will be stored).