Particle Ice Front Interaction - The Brownian Ratchet Model

Michael Chasnitsky\textsuperscript{1}, Victor Yashunsky\textsuperscript{2} and Ido Braslavsky\textsuperscript{1}

\textsuperscript{1}The Robert H Smith Faculty of Agriculture, Food and Environment, The Hebrew University of Jerusalem, Rehovot, Israel and
\textsuperscript{2}Laboratoire PhysicoChimie Curie, Institut Curie,
PSL Research University - Sorbonne Universités, UPMC-CNRS - Equipe labellisée Ligue Contre le Cancer; 75005, Paris, France

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We treat the problem of particle pushing by growing ice as a free diffusion near a wall that moves with discrete steps. When the particle diffuse away from the surface the surface can grow, blocking the particle from going back. Elementary calculations of the model reproduce established results for the critical velocity \( v_c \) for particle engulfment: \( v_c \sim 1/r \) for large particles and \( v_c \sim \text{Const} \) for small particles, \( r \) being the particle’s radius. Using our model we calculate the dragging distance of the particle by treating the pushing as a sequence of growing steps by the surface, each enabled by the particle’s diffusion away. Eventually the particle is engulfed by ice growing around it when a rare event of long diffusion time away from the surface occurs. By calculating numerically the statistics of the diffusion times from the surface and therefore the probability for a such a rare event we calculate the total dragging time and distance \( L \) of the particle by the ice front to be \( L \sim \text{exp}[1/(\eta v^3)] \) where \( \nu \) is the freezing velocity. This relation for \( L \) is confirmed by ours and others experiments. The distance \( L \) provides a length scale for pattern formation during phase transition in colloidal suspensions, such as ice lenses and lamellae structures by freeze casting. Data from the literature for ice lenses thickness and lamellae spacing during freeze casting agree with our prediction for the relation of the distance \( L \). These results lead us to conjecture that lamellae formation is dominated by their lateral growth which pushes and concentrates the particles between them.

\textbf{INTRODUCTION}

When a moving solidification front encounters a foreign particle in the melt, it can either engulf it or push and reject it \cite{1,2}. The outcome of this interaction is fundamental in crystal growth of single crystals \cite{3,4}, soil freezing \cite{5}, alloy casting \cite{6} and freeze casting \cite{7,8,9}.

Ice can only grow when there is water on its surface which then freeze. Having a particle on its surface contradict this basic condition, there are no water on the ice surface where the particle is and ice can not grow there. The particle must be displaced from the surface so its place on the ice surface would be replaced by water in order for the ice to grow (fig 1(a)). It is this mechanism of moving the particle from the surface of ice that is in the heart of the phenomenon of ice-particle interaction.

For high front velocity and large particle size the particle will be engulfed, as oppose to slow velocity and small particle for which the particle can be pushed by the advancing crystallization front. For a given particle size there exist a critical velocity \( v_c \) that separates the two regimes.

Current models of this phenomenon rely on an actual force between the particle and the ice surface which repels the particle. We name these models as force balance models. Our model relies on the particle being free to diffuse and no specific forces between the particle and the surface are involved.

In the literature the interaction of ice surface and a particle is modeled by a “Force Balance Model”. In this model it is agreed that there is a repelling force \( F_d \) between the ice surface and the particle which pushes the particle ahead of the moving front \cite{2}. The pushing force is calculated from Van der Waals interactions and interface shape changes \cite{2}. This pushing force is balanced by a drag force \( F_d \) that pulls the particle toward the solidification front \cite{10}. A steady state of constant velocity particle pushing is than reached when the forces are equal \( F_d = F_d \). From this condition the critical velocity can be estimated to scale as \cite{11}

\begin{equation}
\nu_c \sim \frac{1}{\eta r^3}
\end{equation}

where \( r \) is the particle radius and \( \eta \) is the viscosity of the liquid. Equation \cite{11} is the widely accepted, experimentally verified and intuitive expression for the critical velocity \( v_c \). We’ve omitted here the terms with the film thickness and the surface energies because as we claim that the particle pushing is secondary to a dominant phenomenon of the Brownian ratchet mechanism described below, also they are almost inaccessible experimentally.

\textbf{THE BROWNIAN RATCHET MODEL}

\textbf{Outline of the Model}

We treat the particle as \textit{free} to diffuse and to perform Brownian motion in water near the ice surface. We approximate ice as a wall that the particle can not penetrate. As long as the particle is close to the ice surface,
ice does not grow. Only when the particle is separated at least a distance \( \delta \) from the surface can the ice grow and than the particle is again on the surface (fig 1). There is no treatment in the literature of the case of Brownian motion near ice surface. The x-axes is the time of the simulation which is in units of the number of time steps. A time step is \( 0.1 \cdot T \). Once the particle is over a distance \( \delta \) from the ice surface, ice grows a step.

The Critical Velocity

Now that we have formulated our model, we can calculate the velocity of the particle motion according to the Brownian ratchet model by Peskin, Odell, and Oster [13]. The time to diffuse a distance \( \delta \) is denoted as \( T_\delta \). A freely diffusing particle travels a distance delta on average over time \( T_\delta = \frac{\delta}{\sqrt{2D}} \). For the most simple estimation \[ T_\delta = \tau_\delta \]. After diffusing length \( \delta \), another ice layer is added to the the ice front which means the particle can not go back. Diffusing a larger distance \( L = N\delta \) increases the time linearly with \( N \) \( T_L = N T_\delta \) as appose to \( N^2 \) for regular diffusion. The average speed of the particle is than

\[
v = \frac{L}{T_L} = \frac{\delta}{T_\delta} = \frac{2D}{\delta} \tag{2}
\]

which is perfect ratchet velocity [13]. This would be the speed if the particle would diffuse and ice would grow instantaneously after it. Taking the diffusion coefficient from Einstein-Stokes [15] relation with a correction \( \xi \) [16, 17] for near wall diffusion \( D_{\text{particle}}(r) = \frac{kT}{3\pi\eta r} \) and inserting it into eq. 2 we get the critical velocity for en-

\[
v_c = \frac{\xi kT}{3\pi\eta r_0} \tag{3}
\]

which recovers relation (eq. 1) which is well established and agrees with the previous models. The derivation of the expression for \( v_c \) in eq. 3 is valid only for slow ice growth velocities because than the assumption of instantaneous ice growth is not limited kinetically, i.e. the time \( \frac{T}{v} \) for ice to grow a distance \( \delta \) is much longer than \( \frac{1}{v_c} \) which is the fastest ice can grow planar under specific conditions. Therefore, our model is applicable for ice growth velocity \( v \ll v_0 \) and therefore for large particles \( r \gg r_0 \) (fig 2). Maximum planar growth velocity of ice is estimated under typical conditions to \( v_0 \sim 5 \mu \text{m} / \text{s} \)

Hobbs [18]. Estimating the parameters of eq. 3 with \( kT = 3.17 \cdot 10^{-21} \text{J} \), \( \eta = 1.67 \cdot 10^{-3} \text{Js/m}^2 \), \( \xi = 0.1 \) yields

\[
v_c(r > 15 \mu \text{m}) \approx \frac{24}{(\omega/\mu \text{m}) \cdot (\delta/\mu \text{m})} \text{m/s} \tag{4}
\]

The distance \( \delta \) is expected to be on the scale of the size of an ice layer which is \( \sim 0.5 \text{ nm} \). It is seen that for small particles the limiting factor in the critical velocity for pushing the particle is the growth of ice. Therefore the critical velocity does not depend on the particle size for small particles (fig 2)

\[
v_c(r < 10 \mu \text{m}) \approx v_0 \tag{5}
\]

This independence of the critical velocity on the particle size was observed by Uhlmann, Chalmers, and Jackson [1] in one of the first papers in the field. Rempel and Worster [19] explained such a behavior by the increased surface curvature of the ice surface near the particle for small particles. In our model this behavior follows naturally from the model. This model has another interesting consequence. In the regime where the critical velocity is constant (eq. 5). \( V_0 \) is the maximum velocity ice can grow while staying planar on a very small scale. This
is a parameter that is hard to measure optically (resolution limit) and to the best of our knowledge was never measured.

**Affect Of The Temperature Gradient And The Particle Material** Higher gradient stabilizes the surface \[20\], so we expect for higher gradient the velocity \( V_0 \) will be higher. Also the thermal gradient \( G \) and the thermal conductivities of the liquid, crystal and particle \( \kappa_L, \kappa_C, \kappa_P \) respectively are expected to affect \( \delta = \delta(G, \kappa_L, \kappa_C, \kappa_P) \). \[21, 22\]

### DRAGGING TIME/DISTANCE OF THE PARTICLE BY THE ICE FRONT

In freezing colloidal suspensions the particles are pushed by the freezing front, concentrated and patterns appear. The scaling of this pattern is important in freeze casting, inclusions in steel \[23\] and for ice lenses formation.

Pushing of the particle by ice front is limited in time (and in distance). After being pushed by the ice for a time \( t \) (or a distance \( L = \nu A \cdot t \)), the particle is engulfed. The dragging of the particle is viewed here as a sequence of growing steps by ice \( \{ T_j^\delta \} \) (fig \[1b\]), each one enabled by the diffusion away of the particle to distance \( \delta \). This pushing of the particle is stopped once an event occurs that diffusing a \( \delta \) takes time \( T_{\delta}^{\text{critical}} \gg \delta \) and the particle is engulfed. The total time of the particle dragging is

\[
t = \sum_{i=1}^{N} T_i^\delta = N < T_\delta > = N \frac{\delta}{v}
\]

with \( N \) being the number of steps after which the particle engulfed, i.e. \( T_{\delta}^{N+1} = T_{\delta}^{\text{critical}} \). Next we’d like to get the frequency distribution \( n(T_\delta) \) of the times \( T_\delta \). We perform numerical simulation (fig \[1b\]) of a Brownian motion first passage times with a reflecting boundary at the origin (supplementary). The resulting distribution \( n(T_\delta) \) of the times the particle reaches a distance \( \delta \) from the origin for the first time is shown in figure \[3\] and is best fitted as

\[
n(T_\delta) = \frac{N}{T_{\delta}^{1/2}} \exp(-1.08 \frac{T_\delta}{\tau_\delta})
\]

Engulfment of the particle once a critical event occurs

\[
n(T_{\delta}^{\text{critical}}) \simeq 1
\]

It is reasonable to assume that critical time is proportional to the average diffusing time

\[
T_{\delta}^{\text{critical}} = A \frac{\delta}{v}
\]

, with \( A \sim 5 - 15 \) being an empiric parameter.

![Figure 3: Frequency distribution of the times \( T_\delta \) as a function of \( T_\delta \). The graph summarizes the simulation of Brownian motion shown in figure \[1b\]. Each bin is the number of times that the time to diffuse a distance \( \delta \) was \( T_\delta \). The red line is a fit to the data of equation \[7\], where \( N = 5 \cdot 10^6 \) was the number of times the simulation ran.](image)

Combining equations \[5\], \[6\], \[8\], \[9\] and the definition of \( \tau_\delta \) we get

\[
1 = \frac{t \cdot v}{72 \delta} \exp\left(-\frac{1.08 A \frac{\delta}{v}^2}{2 \nu^2}\right)
\]

than inserting the Einstein-Stokes relation to the diffusion coefficient \( D \), the dragging time \( t \) and distance \( L = \nu \cdot t \) can be expressed as

\[
t = \frac{a \cdot \delta}{v} \exp\left(\frac{1.08 \cdot 2 \cdot A \xi kT}{6 \nu \eta} \frac{1}{\nu \cdot r}\right)
\]

\[
L = \nu \cdot t = a \cdot \delta \exp(1.08 \cdot 2 \cdot A D \frac{1}{\delta} \frac{1}{v}) = \frac{a \cdot \delta}{6 \nu \eta} \exp\left(\frac{1.08 \cdot 2 \cdot A \xi kT}{6 \nu \eta} \frac{1}{\nu \cdot r}\right)
\]

where \( a \) is a parameter we have replaced the numerical constant with. For the case of the interface of water and ice, taking \( T = 273.15 K \), \( \eta = 0.018 \ cm/s \) than

\[
L = a \cdot \delta \exp\left(\frac{240 A \xi}{(\gamma/\mu_m) \cdot (\gamma/\mu_m)}\right)
\]

This relation is verified in experiments where a single particle is dragged by a growing ice surface with constant velocity (fig \[4a\]). Our data and data from Dedovets, Monteux, and Deville \[24\] both agree with equation \[13\]

#### Multi particle systems

This model explains the interaction between a single particle and the interface of ice-water. Most interesting
phenomenon relying on this interaction are in systems with multiple particles interacting with the ice surface, such as ice lens formation \(^5\) and freeze casting \(^8\). In such systems the mutual diffusion coefficient is given by \( D(\phi) = D_0 \hat{D}(\phi) \) where \( D_0 \) is the Einstein-Stokes diffusion coefficient and \( \hat{D}(\phi) \) is a correction which depends on the concentration \( \phi \). Adjusting the diffusion coefficient is the simplest correction to the model to account for the multi-particle system. Instead of inserting \( \hat{D}(\phi) \) as another parameter to equations \( 11 \) and \( 12 \) the definition of \( \xi \) can be altered, so it would be the correction to diffusion which takes particle concentration into account. Under this adjustment the particle dragging distances of multi-particle system should be qualitatively the same as for single particle interacting with the ice front. In figure \( \text{Fig. 4b-d} \) the spacing in the resulting structure from colloidal solution is plotted. The scaling \( L \sim \exp(\frac{1}{v \sqrt{r}}) \) (eq. \( 12 \)) which was derived for single particle dragging is valid for multi-particle systems such as ice lenses growth (fig. \( \text{Fig. 4b} \)) and for lamellae spacing (fig. \( \text{Fig. 4c} \)).

**Lamellae spacing**

The scaling of the lamellae spacing (fig. \( \text{Fig. 4b-d} \)) also obeys the relation \( L \sim \exp(\frac{1}{v \sqrt{r}}) \). This is a surprising result, especially since the agreement is so good. We interpret that as that the formation of the spacing between lamellae is determined by the distance the particles can be pushed between the lamellae. Lateral (with respect to freezing direction) pushing of the particles between the lamellae concentrates the solution.

**Justification of the model validity and assumptions**

Diffusion near a wall is highly damped \(^{10}\) due to the friction (no-slip boundary condition) of the liquid near the wall. The damping scales as \( \frac{\xi}{d} \) depends on the thickness \( d \) of the liquid layer between the particle and the wall. \(^1, 10\) This dependence of the diffusion coefficient \( \frac{\partial D}{\partial z} > 0 \) on the distance from the surface \( z \) results in drift away from the surface \(^{28, 51} \). In our model we assume the distance between the particle and the ice surface is roughly on the molecular scale and the variation in \( D \) can be neglected, so \( D \) is assumed to be independent of \( z \).

According to hydrodynamic calculations \(^{10, 10} \) the diffusion coefficient of a particle near the ice surface should vanish. Our model deals with distances between the particle and the surface of ice being on the molecular level, it is unclear whether the hydrodynamic approach is valid in this limit. The thing to notice is that when the particle fluctuates away from the surface under pressure is created between the particle and the surface which must be filled with water molecules at the same rate that ice grows. The water molecules can be supplied there by surface diffusion or by lubrication flow \(^{10} \) on the interface between ice and the particle. The thickness of the liquid film between the particle and the ice surface was considered to be from a molecular size \(^1\) up to 10 nm \(^{10}\). In both cases, for both thicknesses it was considered that water can fill the gap between the particle and the ice sufficiently fast so ice could grow in microns per second.

![Image of lamellae spacing](image-url)

**Figure 4**: (a) The dragging distance of oil droplets (○) and glass beads (▼) for different freezing velocities. The lines are fits of equation \( 13 \) with \( r = 10 \) and 22 \( \mu m \), \( A\xi = 0.59 \) and 0.17, \( \delta = 1.9 \) and 0.2 \( nm \), \( n = 357 \) and 0.1 respectively. (b) (■) The thickness of the ice lenses formed during directional freezing of a colloidal solution of water and monodispersed glass beads. The y-axes are logarithmic in all graphs. In the insets the x-axes is the reciprocal of the main graph x-axes. A straight line in the inset corresponds to an agreement with our model \( L \sim \exp(\frac{1}{v \sqrt{r}}) \) (eq. \( 12 \)). We see that the model (eq. \( 12 \)) describes the data well. The data is taken from Dedovets, Monteux, and Deville \(^{24} \) for the oil droplets (○) and from Saruya, Kurita, and Rempel \(^{27} \) for ice lenses growth (■). The data for the glass beads (▼) was measured using a standard directional freezing setup for this study \(^{28} \). (c-d) The lamellar spacing as a function of the freezing velocity \( v \) (c) and \( \frac{1}{v} \) (d). The structures formed during freeze casting experiments for different freezing velocities of a solution of water with 0.8 \( \mu m \) diameter alumina particles at different volume concentrations in the of 5-30 %. Different temperature of the cooling plate were used -10, -20, -30 and -50 C, which represent different thermal gradients at the interface. The data for the freeze casting structures (c-d) is taken from Waschkies, Oberacker, and Hoffmann \(^{24} \).
Our model, as stated above, is the simplest approximation of the phenomenon with the parameter $\xi$ being the correction term to the diffusion taking these considerations into account.

CONCLUSIONS AND OUTLOOK

The Brownian ratchet explains the mechanism behind the particle pushing by the ice surface. We show here a mechanical model of how ice is pushing particles. Using the model we have derived a relation between the distance of the particle pushing and the particle size and freezing velocity $L \sim \exp\left(\frac{1}{\sqrt{v}}\right)$ (eq. 12). We showed that this scaling can be also used to estimate length scales in patterns resulting from ice freezing and phase transition in general of colloidal solutions. Using the data from Waschkies, Oberacker, and Hoffmann [20] we saw that the lamellae spacing scales in the same way, which leads us to conjecture that lamellae formation is driven by the pushing of particles and not the surface instabilities on ice [20]. We conjecture that the instability on the ice surface grows ahead and starts to deform, loosing memory of its initial structure and consequently a cellular structure emerges by pushing the particles laterally between the cells.

It would be very interesting to see under which other conditions, such as different particle concentrations in multi particle systems, gravity and liquid flow relation [12] is still valid. Obviously modifications to the model would be necessary to properly describe and to account for these conditions. This model provides a simple framework which can be further developed to describe solution freezing.

This model and this approach should be interesting for the problem of membrane rupturing and consequently cell and tissue damaging by growing ice. There ice grows until it approaches the membrane. Then ice can no longer grow since there are no water available for freezing between the ice and the membrane and we might naively think that the cell is saved at this point. However, experiments show that ice can grow into cells and rupture membranes under these conditions [12]. A similar model to ours may be proposed where the thermal fluctuations of the membrane play the same role as the particle’s Brownian motion in our model. The membrane fluctuations create a separation between the membrane and the ice surface to allow ice to grow toward the membrane. Once ice grows the membrane can return to its initial state and with each such cycle it has a strain and tension build up that eventually cause the membrane to rupture resulting in a catastrophe for the cell.

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