Two-dimensional description of surface-bounded exospheres with application to the migration of water molecules on the Moon

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On the Moon, water molecules and other volatiles are thought to migrate along ballistic trajectories. Here, this migration process is described in terms of a two-dimensional partial differential equation for the surface concentration, based on the probability distribution of thermal ballistic hops. A random-walk model, a corresponding diffusion coefficient, and a continuum description are provided. In other words, a surface-bounded exosphere is described purely in terms of quantities on the surface, which can provide computational and conceptual advantages. The derived continuum equation can be used to calculate the steady-state distribution of the surface concentration of volatile water molecules. An analytic steady-state solution is obtained for an equatorial ring; it reveals the width and mass of the pileup of molecules at the morning terminator.

DOI: 10.1103/PhysRevE.91.052154

PACS number(s): 05.40.Fb, 05.60.Cd, 96.12.Jt, 96.20.-n

I. INTRODUCTION

Recently, there has been considerable interest in volatiles on the Moon and Mercury. The Moon, Mercury, the largest asteroids, and the big satellites of the giant planets have enough gravity to hold on to most molecular species, including H_2O , at thermal speeds. Surface-bounded exospheres are thought to consist of molecules that hop in ballistic trajectories until either lost to space or captured in permanent cold traps [1–4]. The kinetic behavior of these molecules is determined by their interaction with the surface rather than with each other (exospheres are by definition collisionless). Hence, it is natural to describe them in terms of surface quantities alone.

Highly volatile atoms, such as helium on the Moon [5,6], can hop on the day and the night side, while less volatiles species, such as H_2O , will freeze to the surface at night and only migrate on the day side. The presence of a transient or dilute water exosphere is surmised based on the presence of ice deposits in permanently shadowed craters near the rotational poles. Potential time variability in a lunar water exosphere has been suggested by tantalizing observations (see, e.g., [7]).

Up to now, computer model calculations have been based on individual particles that are launched with a Maxwellian speed distribution in a random direction [3,8-11]. Figure 1 shows the result of one such model calculation. Water molecules undergo ballistic flights on the day side and rest on the surface on the night side. Also noticeable is a pileup in the surface concentration near the morning terminator, due to a snow plow effect. As the sun rises, many molecules hop back to the night side.

The goal here is to describe the lateral mass flux of the hopping molecules in a continuum approximation, which takes the form of a partial differential equation on a sphere for the surface density σ of H₂O molecules. A continuum description of lateral fluxes in the terrestrial exosphere, which is bounded by an exobase instead of a rigid surface, has been considered previously (see, e.g., [12,13]). The behavior with height is also of interest [14], but the goal here is to eliminate the vertical dimension from the governing equations. Such a formulation

can have computational advantages, e.g., when the surface density varies by many orders of magnitude over the globe. But this paper will be restricted to the derivation of the equation and an analytic solution to a reduced and simplified version of these equations. A broader goal is to call attention to this randomwalk problem, which has gained significant importance in its field, for a community beyond planetary science.

II. THERMAL BALLISTIC HOPS

A. Problem setup

A molecule thermalizes when in contact with the surface and leaves in a random direction. Hence its migration can be described as a memoryless stochastic process (a Markov process) of discrete movements.

A molecule of mass m acquires thermal energy on the surface with temperature T, leaves with a Maxwellian velocity distribution, and hops under the influence of gravitational acceleration g on a surface with horizontal coordinates x and y, or alternatively geographic latitude and longitude.

The hop length is assumed to be small compared to the radius of the body, such that curvature effects can be neglected. Ballistic flight can also be calculated for nonuniform gravity, but this is merely more technical [15]. We also assume that the time of flight is short compared to the rotation period of the body, which is an excellent approximation when the typical time of flight is a few minutes.

B. Probability distribution of thermal ballistic hops

Elementary mechanics provides the distance *r* of a ballistic hop with initial velocity (v_x, v_y, v_z) ,

$$r = \frac{2}{g} v_z \sqrt{v_x^2 + v_y^2}$$
(1)

and the time of flight,

$$\tau = \frac{2v_z}{g}.$$
 (2)

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FIG. 1. (Color) Results of a Monte Carlo model calculation of water molecules hopping on the lunar surface. Black molecules reside on the surface and blue molecules are in flight. Color contours represent surface temperature. The globe spins counterclockwise. The concentration of water molecules is enhanced near the poles and near the morning terminator. Water molecules are generated in the subsolar region, destroyed by photodissociation during flight, and some are trapped near the poles. The model is described in Ref. [11].

The Maxwell probability distribution for one component of the velocity is

$$f(v) = \sqrt{\frac{m}{2\pi kT}} e^{-\frac{mv^2}{2kT}}$$
(3)

with the simple exception that vertical velocities can only be upward, such that the probability distribution of v_z is not $f(v_z)$ but $2f(v_z)$. Combining (1) and (3), the average flight distance is

$$\overline{r} = \iiint rf(v_x)f(v_y)2f(v_z)dv_xdv_ydv_z = \frac{2kT}{mg}$$
(4)

and the average flight time is

$$\overline{\tau} = \iiint \tau f(v_x) f(v_y) 2f(v_z) dv_x dv_y dv_z$$
$$= \frac{2}{g} \sqrt{\frac{2kT}{\pi m}} = 2\sqrt{\frac{\overline{r}}{\pi g}}.$$
(5)

The combination kT/mg may be interpreted as the scale height H of the exosphere. For example, $\overline{r} = 2H$.

The probability density p(x, y) that molecules leave from coordinate (0,0) and end up at location (x, y) after one hop is

$$p(x,y) = \iiint f(v_x)f(v_y)2f(v_z)$$
$$\times \delta\left(x - \frac{2}{g}v_z v_x\right)\delta\left(y - \frac{2}{g}v_z v_y\right)dv_x dv_y dv_z, \quad (6)$$

where δ is the Dirac delta function. The result of the integrals is

$$p(x,y) = \frac{1}{4\pi H \sqrt{x^2 + y^2}} e^{-\frac{1}{2H}\sqrt{x^2 + y^2}}.$$
 (7)

It can be verified that this probability distribution is normalized and reproduces the mean flight distance (4),

$$\iint p(x,y) \, dx \, dy = 1, \tag{8}$$

$$\bar{r} = \iint p(x,y)\sqrt{x^2 + y^2} \, dx \, dy = \frac{2kT}{mg} = 2H.$$
 (9)

The probability distribution of hop lengths follows from (7) and is exponential,

$$p(r) = \frac{1}{2H} e^{-r/(2H)}.$$
 (10)

The hop duration τ also has a probability distribution, not derived here, and r and τ are correlated.

C. Random-walk model and diffusion coefficient

As a digression to the main line of thought, we consider a sequence of hops as a random walk and the analogous description in terms of a diffusion process. The variance of the hop length can be calculated from (10) and is $\overline{r^2} = 2\overline{r}^2$, and it is obviously finite. It is possible to define a diffusion coefficient

$$D = \frac{\overline{r^2}}{2\overline{\tau}} = \frac{\overline{r}^2}{\overline{\tau}}.$$
 (11)

(Such an association has already been made by Hodges [12] for an exosphere with an exobase instead of a rigid surface. His result was $D = H\overline{|v|}$.)

On cold surfaces, the surface residence time is no longer negligible compared to the duration of flight, and the time τ should be the in-flight time plus the residence time. For example, at 120 K, a temperature found on the nightside of the Moon, the (extrapolated) sublimation rate of ice is $1 \times 10^{13} \text{ mol/m}^2/\text{s}$ and $\tau = 1 \times 10^6 \text{ s}$ or about 2/5 of the lunar day. The surface residence time depends very strongly on temperature, and if the migration is dominated by residence time, the temperature (spatial) dependence of *D* must not be neglected.

Values for *D* and other relevant parameters are shown in Table I. Mercury and the Moon have about the same diffusion constant at the subsolar point, because the difference in gravity is nearly compensated by the difference in surface temperature.

A random walk of discrete hops is described by a diffusion process with the same diffusion coefficient D. For example, for the distance d traveled,

$$d^2 = 2Dt. \tag{12}$$

Figure 2 shows that this is an excellent approximation. This is not necessarily the case for other moments, such as \overline{d} . Nevertheless, (12) can be used to estimate that it takes about 9 h on the dayside of the Moon to travel a distance $\pi R/2$, from the subsolar point to the night terminator.

TABLE I. Parameters relevant for thermal ballistic hops of H₂O molecules: Surface acceleration g, mean hop length \overline{r} (4), mean flight duration $\overline{\tau}$ (5), diffusion coefficient D (11), and ratio of hop length to the radius R of the body. Unless noted otherwise, surface temperature T is calculated for the subsolar point at the semimajor axis and for an albedo of 0.1, which represents a maximum surface temperature for this distance from the Sun. The surface residence time $\overline{\tau}_{res}$ is a rough estimate based on the equilibrium vapor pressure of ice [16].

	$g (m^2/s)$	Т (К)	<i>r</i> (km)	$\overline{\tau}$ (s)	$\overline{\tau}_{\rm res}$ (s)	D (km^2/s)	\overline{r}/R
Mercury	3.7	617	154	230	2×10^{-11}	103	0.06
Moon	1.62						
subsolar		384	219	415	3×10^{-9}	115	0.13
dayside		340	194	390	3×10^{-8}	96	0.11
nightside		120	68	231	1×10^{6}	0.005	0.04
Ceres	0.27	231	788	1930	4×10^{-5}	322	1.6
Ganymede	1.43	168	109	311	0.6	38	0.04

Definition of a diffusion coefficient also allows for the association with a diffusion equation

$$\frac{\partial \sigma}{\partial t} = \nabla \cdot (D\nabla \sigma) \,. \tag{13}$$

The description (and abstraction) in terms of a diffusion coefficient represents a significant generalization of the problem. The vertical dimension is eliminated, individual hops do not need to be distinguished from a series of hops, and in-flight time does not need to be distinguished from surface residence time. It is (at least to low order) applicable to all of this.



FIG. 2. Root-mean-square distance traveled after a time t, based on (a) probabilistic time steps, Eqs. (1)–(3), (b) time steps of fixed size (4) and duration (5) but random direction, and (c) the simple square-root law (12) with diffusion coefficient (11). For the calculation of (a) and (b), 2000 random walks each were averaged, which retains small wiggles in the behavior. For case (a), times were rebinned for this plot.

III. CONTINUUM FORMULATION

A continuum approximation provides a coarse-grained description for spatial scales larger than the hop length. For H_2O on the Moon, these are spatial scales longer than a few hundred km.

A. Derivation of a continuum equation for thermal ballistic hops

The influx to location (0,0) from all surrounding areas is

$$I(0,0) = \iint E(x,y)p(x,y)\,dx\,dy,\tag{14}$$

where E is the number of water molecules that leave the surface per area and per time (a sublimation rate). This integral can be converted into a differential expression using a Taylor expansion of E,

$$E(x,y) = E(0,0) + \frac{\partial E}{\partial x}x + \frac{\partial E}{\partial y}y + \frac{\partial^2 E}{\partial x^2}\frac{x^2}{2} + \frac{\partial^2 E}{\partial x \partial y}xy + \frac{\partial^2 E}{\partial x^2}\frac{y^2}{2}, \quad (15)$$

where all derivatives are evaluated at (0,0). All odd terms vanish upon integration in (14), and thus

$$I(0,0) = E(0,0) + \frac{1}{2} \iiint \left(\frac{\partial^2 E}{\partial x^2} x^2 + \frac{\partial^2 E}{\partial y^2} y^2 \right) p(x,y) \, dx \, dy$$

$$= E(0,0) + \frac{1}{2} \frac{\partial^2 E}{\partial x^2} \iint x^2 p(x,y) \, dx \, dy$$

$$+ \frac{1}{2} \frac{\partial^2 E}{\partial y^2} \iint y^2 p(x,y) \, dx \, dy.$$
(16)

Using (7), it can be shown that

$$\iint x^2 p(x, y) \, dx \, dy = (2H)^2 = \overline{r}^2. \tag{17}$$

By symmetry, the same result is obtained when integrating over y^2 . Thus (16) becomes

$$I(0,0) - E(0,0) = \frac{\overline{r}^2}{2} \left(\frac{\partial^2 E}{\partial x^2} + \frac{\partial^2 E}{\partial y^2} \right) = \frac{\overline{r}^2}{2} \nabla^2 E. \quad (18)$$

Equation (18) states that the incoming flux is the outgoing flux plus a Laplacian term. In other words, the change in H₂O concentration, $\partial\sigma/\partial t = I - E$, is

$$\frac{\partial \sigma}{\partial t} = \frac{\overline{r}^2}{2} \nabla^2 E(\sigma, T) = 2H^2 \nabla^2 E(\sigma, T).$$
(19)

Here *E* is expressed not in terms of *x* and *y* but in terms of σ and *T*.

Since the derivation did not include time of flight, this equation is not suitable for studying the spread of an episodic source, as is (13). Instead, the equation is appropriate for the steady-state distribution of σ . It does not (yet) include any sources, such that there is no steady-state solution with cold traps. It describes the geographic pattern of surface concentration, as ever migrating water molecules react to a changing temperature environment caused by the rotation of the body.

We expect a steady-state solution for σ that is constant relative to solar illumination, not relative to the physical surface. Hence, the time change has an advective component, and the PDE for the steady state is

$$w \cdot \nabla \sigma = \frac{\overline{r}^2}{2} \nabla^2 E(\sigma, T),$$
 (20)

where w is the constant advection velocity due to the rotation of the Moon relative to solar illumination, essentially in the longitude direction.

B. Quantification of E

The sublimation rate *E* is a function of both temperature *T* and the surface density of water molecules, σ . For physical reasons, E(0,T) = 0 and $E(\infty,T) \equiv E_{\infty}(T)$, where E_{∞} is the sublimation rate of pure ice [17,18],

$$E_{\infty}(T) = p_e(T) \sqrt{\frac{m}{2\pi kT}},$$
(21)

and p_e is the equilibrium vapor pressure of ice [19]. Given the scarcity of laboratory data, a separation of variables is a reasonable approximation,

$$E(\sigma, T) = E_{\infty}(T)f(\sigma).$$
(22)

A simple conceptual parametrization is

$$f = \min(\sigma/\sigma_0, 1), \tag{23}$$

where σ_0 is the density of a monolayer; for small σ , *E* becomes proportional to σ . Measurements of adsorption isotherms of lunar grains have been used to approximate $f(\sigma)$ [20], but here we will use (23).

In (19), the accumulation rate is given by the twodimensional Laplacian of the emission rate E. Where E has a local minimum, more water will accumulate. As σ increases, E will saturate at $E_{\infty}(T)$, and if the temperature is low, it can remain a local minimum, and water will continue to accumulate indefinitely. This corresponds to a cold trap.

C. Application: One-dimensional steady-state distribution

The one-dimensional version of (20) is

$$w\frac{d\sigma}{d\tilde{x}} = \frac{\bar{r}^2}{2} \frac{d^2 E(\sigma, T)}{d\tilde{x}^2}$$
(24)

defined on an equatorial circle. We can measure distance in degree longitude rather than meters, such that \tilde{x} becomes an angle, w an angular velocity, and so on.

Without advection, w = 0, the left-hand side of (24) is zero. Given the periodic domain, this implies that *E* is constant. In this case, σ and *T* are directly related, $\sigma = \sigma(T)$; large *T* corresponds to small σ .

With advection, $w \neq 0$, the solution is qualitatively different. Integrating (24) once,

$$w\sigma = \frac{\bar{r}^2}{2} \frac{dE(\sigma, T)}{d\tilde{x}} + C.$$
 (25)

Integrating over the whole periodic domain,

$$2\pi C = w \int_0^{2\pi} \sigma \, dx = wM, \qquad (26)$$

where we define the total mass as M. Hence,

$$\sigma(\tilde{x}) = \frac{\overline{r}^2}{2w} \frac{dE(\sigma, T)}{d\tilde{x}} + \frac{M}{2\pi}.$$
 (27)

Using separation of variables for E (22) and the simple form (23), $E = E_{\infty}(T)\sigma/\sigma_0$. We seek a solution where $\sigma < \sigma_0$ everywhere, such that (25) becomes

$$0 = \frac{1}{\beta} E_{\infty} \sigma' + \left(\frac{1}{\beta} E_{\infty}' - 1\right) \sigma + \frac{M}{2\pi}, \qquad (28)$$

where $\beta = 2w\sigma_0/\overline{r}^2$.

Suppose E_{∞} (and hence temperature) is piecewise constant, with one temperature on the dayside and another on the nightside. Then, on each of the two pieces,

$$0 = \lambda \sigma' - \sigma + \frac{M}{2\pi},$$
(29)

where λ is a length scale,

$$\lambda = \frac{\bar{r}^2}{2w} \frac{E_\infty}{\sigma_0}.$$
(30)

The solution to (29) is

$$\sigma = \frac{M}{2\pi} (1 + C e^{\tilde{x}/\lambda}). \tag{31}$$

Equation (31) is valid on the nightside, with coefficients C_n and λ_n , and on the dayside, with coefficients C_d and λ_d .

Across the night-day boundary, $\sigma E_{\infty} = \text{const}$ (and therefore σ will be discontinuous where the temperature has a discontinuity). Choosing the location of the evening terminator at $\tilde{x} = 0$ and that of the morning terminator at $\tilde{x} = \pi$,

$$\sigma_n(0)E_n = \sigma_d(2\pi)E_d, \qquad (32a)$$

$$\sigma_n(\pi)E_n = \sigma_d(\pi)E_d. \tag{32b}$$

Using (31), this leads to

$$(C_n + 1)E_n = (C_d e^{2\pi/\lambda_d} + 1)E_d,$$
 (33a)

$$(C_n e^{\pi/\lambda_n} + 1)E_n = (C_d e^{\pi/\lambda_d} + 1)E_d,$$
 (33b)

and the cumbersome coefficients

$$C_n = \left(\frac{E_d}{E_n} - 1\right) \frac{e^{\pi/\lambda_d} - 1}{e^{\pi(\frac{1}{\lambda_n} + \frac{1}{\lambda_d})} - 1},$$
(34a)

$$C_{d} = \left(\frac{E_{n}}{E_{d}} - 1\right) \frac{e^{\pi/\lambda_{n}} - 1}{\left[e^{\pi(\frac{1}{\lambda_{n}} + \frac{1}{\lambda_{d}})} - 1\right]e^{\pi/\lambda_{d}}}.$$
 (34b)

Within our approximations, $E_d/E_n = \lambda_d/\lambda_n$. In the limits $\pi \ll \lambda_d$ and $\pi \gg \lambda_n$,

$$C_n \approx \frac{\pi}{\lambda_n} e^{-\pi/\lambda_n},$$
 (35a)

$$C_d \approx -1 + \frac{2\pi}{\lambda_d}.$$
 (35b)

Using (31), the final approximate solutions are

$$\sigma_n = \frac{M}{2\pi} \left(1 + \frac{\pi}{\lambda_n} e^{(\tilde{x} - \pi)/\lambda_n} \right), \quad 0 > \tilde{x} > \pi, \quad (36a)$$

$$\sigma_d = \frac{M}{2\pi} \frac{2\pi - \tilde{x}}{\lambda_d} \approx 0, \quad \pi > \tilde{x} > 2\pi.$$
(36b)

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FIG. 3. Analytic solution to the simplified one-dimensional problem as a function of local time (or geographic longitude). The surface density of H₂O, σ , is normalized to the average density.

Figure 3 shows the solution for $\lambda_n = 3^\circ$ (91 km). It reveals a nearly constant $\sigma = M/2\pi$ over most of the nightside $(0, ..., \pi)$, an exponential increase before sunrise (π) , and $\sigma \approx 0$ on the dayside $(\pi, ..., 2\pi)$. Even this simple model reproduces the dusk-dawn asymmetry [11], with a high concentration near the morning terminator, but not at the evening terminator (Fig. 1). (In reality, this pileup continues slightly into the dayside as the surface needs time to heat up [11]).

The normalization of (36a) is $\int_0^{\pi} \sigma_n d\tilde{x} = M$. Almost no mass resides on the dayside, half is spread out uniformly along the nightside, and half is concentrated within a few λ_n of the morning terminator. Essentially all of the dayside's worth of water is piled up behind the morning terminator.

We learn two things about the pileup part of the solution. First, the pileup contains about half of the entire mass. Second, the length scale for the pileup is

$$\lambda_n = \frac{\overline{r}^2}{2w} \frac{E_n}{\sigma_0}.$$
(37)

This length scale convolves several physical effects: \overline{r} is the average hop distance of molecules, w is the rotation speed of the Moon (or, more accurately, that of its terminator), and E_n is the sublimation rate of ice on the nightside. This last quantity appears, because it steadily smooths the concentration distribution on the nightside. (If the nightside becomes so cold that migration is slow relative to the length of the night, the assumptions of this derivation break down and the width will simply be \overline{r} . This may be marginally the case for the Moon).

D. Generalizations of the PDE

Sinks or sources can be added to (19),

$$\frac{\partial \sigma}{\partial t} = (\text{sources}) - (\text{sinks}) + \frac{\overline{r}^2}{2} \nabla^2 E.$$
 (38)

Examples of sources are water-bearing dust particles or icy bodies that fall onto the surface or water molecules produced chemically by interaction with the solar wind. Examples of sinks are in-flight photodissociation (on the dayside) and gravitational escape, the former being substantial and the latter being negligible for the Moon. A cold trap is not a sink; it is represented by an area where ice accumulates and *E* becomes independent of σ .

An in-flight destruction probability β can be implemented by replacing p in (14) with $p \exp(-\beta)$. By the same approximation, the normalization (8) is no longer unity but $\exp(-\beta)$. With that, Eq. (18) becomes

$$I = e^{-\beta}E + \frac{\overline{r}^2}{2}e^{-\beta}\nabla^2 E.$$
 (39)

To first order in β , Eq. (19) becomes

$$\frac{\partial \sigma}{\partial t} = (1 - \beta) \frac{\overline{r}^2}{2} \nabla^2 E - \beta E.$$
(40)

The equation for the steady-state distribution is

$$w \cdot \nabla \sigma = (\text{sources}) + (1 - \beta) \frac{\overline{r}^2}{2} \nabla^2 E - \beta E.$$
 (41)

IV. CONCLUSIONS AND PROSPECTS

Ensembles of thermal ballistic hops are described as random walks and, separately, as a continuum process on the surface of a sphere. Evidently, ballistic hops represent a random walk on a sphere (equivalent to an event-driven computational method). This random walk can be described in terms of thermally driven hops of stochastic length and duration, Eqs. (1) and (2), but is also well described by hops of average length (4), average duration (5), and random launch direction. Computationally, a two-dimensional random walk is much simpler than three-dimensional ballistic hops. Three random variables (3) are used to calculate the new geographic coordinates, and if residence time τ_{res} is non-negligible a fourth random number is involved.

Furthermore, Eq. (11) associates the random walk with a diffusion coefficient and thus with a two-dimensional diffusion equation, which provides (at the minimum) a low-order continuum description of the migration process.

Equation (20) is the continuum formulation for the steadystate solution on a rotating sphere, generalized in (41) to include loss during migration. Figure 3 shows an approximate analytic solution for an equatorial ring, which reproduces the pileup of water molecules at the morning terminator, which contains half the mass and has a width determined by a combination of physical parameters (37). Solutions to the two-dimensional steady-state equations (20) or (41) would be even more insightful.

Solving the following open problems would be most useful to the study of surface-bounded exospheres:

(i) Does a two-dimensional diffusion equation, as in (13), exactly describe random walks of thermal ballistic hops? (Note that hop length and hop duration are correlated). And how does the first moment of d, \overline{d} , depend on time?

(ii) What is the steady-state solution for the surface concentration and exosphere density? Even without any loss process, this solution is nontrivial. Note that any longitudinal dependence implies diurnal variation. NORBERT SCHORGHOFER

(iii) What fraction of water molecules is captured in polar cold traps as a function of cold trapping area and photodestruction rate? This is a first-passage problem. And is there a significant tail in the distribution of molecular lifetimes, due to molecules that hide on the nightside over consecutive months?

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