Thermodynamics of Surface-Bounded Exospheres: Divergent Near-surface Density

Norbert Schörghofer

1Planetary Science Institute, Tucson, Arizona*

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ABSTRACT

The exospheres of the Moon, Mercury, and several other solar system bodies consist of an ensemble of ballistic hops. Here, I derive the vertical density profile of a stationary surface-bounded exosphere with a fixed number of particles. The density approaches infinity near the surface, a property that is inconsistent with the widely used concept of a barometric exosphere. The result explains a previously unexplained feature of the Mercurian hydrogen exosphere. Vertical density profiles that were interpreted as a superposition of a hot and a cold (ground hugging) population are in fact consistent with a population at a single temperature. A ground-hugging population is a robust feature of a one-component surface-bounded exosphere, and only probability distributions that are strongly biased against relatively small launch velocities would not exhibit a near-surface divergence in the density profile.

Keywords: planets and satellites: atmospheres — planets and satellites: individual (Moon, Mercury)

1. INTRODUCTION

The Moon, Mercury, and several other solar system bodies have rarefied atmospheres, which are collisionless exospheres (e.g., H, H₂, He, Na, Ar, and maybe H₂O) (Killen & Ip 1999). The classical theory of surface-bounded exospheres holds that molecules and atoms follow ballistic trajectories and those that fall back take on the temperature of the surface, leave with a thermal velocity distribution, and undergo a sequence of ballistic hops (Watson et al. 1961; Killen & Ip 1999; Schorghofer 2017). This type of exosphere—surface-bounded, thermalized, and with a limited supply—is relevant to recent and upcoming measurement campaigns, such as by the LADEE (Lunar Atmosphere Dust and Environment Explorer) spacecraft and the PekiColombo mission to Mercury. The details of the vapor-solid interactions have been debated extensively, and are still inconclusive (e.g., Hodges 1980, 2002; DeSimone & Orlando 2014; Kegerreis et al. 2017). The validity of the classical theory will be increasingly put to the test thanks to observational and laboratory measurements. However, there is a more basic problem, namely that the properties of a surface-bounded exosphere have not been worked out properly. Here, I significantly revise previous theoretical results, and in the process explain a puzzling feature of the Mercurian (Hermean) exosphere.

Exospheres above a dense atmosphere, such as on Earth and the Sun, have long been investigated theoretically (Öpik & Singer 1959, 1961; Chamberlain 1963; Shen 1963). Joseph Chamberlain provided a Liouville theorem style argument that an exosphere, although collisionless, should obey the barometric law. For the simple case of constant gravitational acceleration $g$, the density follows an exponential dependence

$$\rho(z) = \rho(0)e^{-z/H}$$ (1)

where $z$ is the height above the surface (or exobase) and $H$ the scale height:

$$H = \frac{kT}{mg}$$ (2)

where $k$ is the Boltzmann constant, $T$ the temperature associated with the initial velocities, and $m$ the mass of the atom or molecule. This is the same scale height as that of an isothermal hydrostatic atmosphere, and eq. (1) is the “barometric law”, and in the context of an exosphere often referred to as (the simplest form of) the “Chamberlain distribution”.

Although originally derived for an exobase, the concept of a barometric exosphere has been extensively applied to the situation where the base of the exosphere...
is a solid surface. One significant difference is that an exobase functions as a reservoir so the population of exospheric particles is not a closed system. Rather than build on previous theory of questionable applicability, I use an approach that is ideally suited for the surface-bounded case and fully analytically tractable.

A single ballistic hop. Let \( v_z \) denote the initial vertical velocity component. It follows from elementary mechanics that the duration of ballistic flight is

\[
t_D = \frac{2v_z}{g}
\]

and the maximum height of a ballistic trajectory is

\[
z_{\text{max}} = \frac{v_z^2}{2g}
\]

The vertical velocity as a function of time and height, respectively, is

\[
dz &= v_z - gt = \sqrt{v_z^2 - 2gz}
\]

The time the particle spends at a particular height \( z \) is proportional to \( 1/dz/dt \). Therefore, the density profile for a single ballistic hop (6) is

\[
\rho(z) = \frac{g}{v_z} \frac{1}{\sqrt{v_z^2 - 2gz}}
\]

where the prefactor is determined from normalization,

\[
\int_0^{z_{\text{max}}} \rho(z) \, dz = 1
\]

In particular, \( \rho(0) = g/v_z^2 \), so for a probability distribution of launch velocities that does not vanish for small \( v_z \), the density at the surface becomes infinite, in stark contrast to the barometric behavior.

2. THERMODYNAMIC AVERAGES

Ensemble averages. Given a probability distribution of initial velocities \( P(v_z) \), the ensemble average of a quantity \( X \) per hop is

\[
\langle X \rangle = \int XP(v_z) \, dv_z
\]

Next we consider a sequence of hops with surface residence times much shorter than the time of flight. Although an exosphere is collisionless, the trajectories still represent a thermodynamic ensemble (i.e., a statistical ensemble in equilibrium), as the particles thermalize with the surface. The ensemble average of a quantity \( X \) at a given time, denoted by \( \langle \rangle \), has to be weighted by the flight duration and is

\[
\langle X \rangle = \int XP(v_z) \frac{t_D}{\langle t_D \rangle} \, dv_z
\]

\[
= \int XP(v_z) \frac{v_z}{\langle v_z \rangle} \, dv_z
\]

\( \langle X \rangle \) is the time average of a stationary situation, or, with enough particles, a snapshot. Both types of averages are properly normalized: \( \langle 1 \rangle = 1 \) and \( \langle 1 \rangle = 1 \).

Divergence at the surface. Equations (6), (8), and (9b) imply

\[
\langle \rho(0) \rangle = g \int_0^\infty \frac{1}{v_z^2} P(v_z) \, dz
\]

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\]

When the probability distribution is expanded for small \( v_z \) as \( P(v_z) \propto v_z^n \), then \( \langle \rho(0) \rangle < \infty \) requires \( n > 1 \) and \( \langle \rho(0) \rangle < \infty \) requires \( n > 0 \). For a Boltzmann distribution (an exponential) \( n = 0 \), so both diverge.

Equipartition. The equipartition theorem applied to the vertical launch velocity is

\[
\frac{m \langle v_z^2 \rangle}{2} = \frac{kT}{2}
\]

Quantities that are given by \( \langle v_z^2 \rangle \) can be calculated irrespective of the initial velocity distribution. The average height (4) of a hop is

\[
\langle z_{\text{max}} \rangle = \frac{\langle v_z^2 \rangle}{2g} = \frac{kT}{2mg} = \frac{H}{2}
\]

The time-averaged height for a single ballistic hop is

\[
\int_0^{z_{\text{max}}} z \rho(z) \, dz = \frac{v_z^2}{3g} = \frac{2}{3} z_{\text{max}} = \frac{H}{3}
\]

and the ensemble average is also

\[
\langle z \rangle = \frac{\langle v_z^2 \rangle}{3g} = \frac{H}{3}
\]

The scale height is three times smaller than for a barometric exosphere at the same temperature. The barometric law is inconsistent with equipartition of energy during solid-vapor interaction on the surface. The divergence and scale-height argument each suggest that surface-bounded exospheres are more concentrated toward the surface than the Chamberlain solution.

Maxwell-Boltzmann distribution. The Boltzmann distribution of the vertical velocity component \( v_z \) is

\[
P_M(v_z) = 2\sqrt{\frac{s}{\pi}} e^{-sv_z^2} \quad \text{with} \quad s = \frac{m}{2kT} = \frac{1}{2gH}
\]

which has averages

\[
\langle v_z \rangle = \frac{1}{\sqrt{\pi s}}, \quad \langle v_z^2 \rangle = \frac{1}{2s} = \frac{kT}{m}, \quad \langle v_z^3 \rangle = \frac{1}{\sqrt{\pi s^3}}
\]

\[
\langle v_z \rangle = \frac{1}{\sqrt{\pi s}}, \quad \langle v_z^2 \rangle = \frac{1}{s}
\]
The averages of \( t_D \) and \( z_{\text{max}} \), using eqs. (3), (4), (8), and (9b) are

\[
\langle t_D \rangle = \frac{2}{g} \langle v_z \rangle = \sqrt{\frac{8H}{g\pi}} \quad \text{(18a)}
\]

\[
\langle t_D \rangle = \frac{2}{g} \langle v_z \rangle = \sqrt{\frac{2H\pi}{g}} = \frac{\pi}{2} \langle t_D \rangle \quad \text{(18b)}
\]

\[
\langle z_{\text{max}} \rangle = \frac{1}{g^2 \langle t_D \rangle} \langle v_z^3 \rangle = H \quad \text{(18c)}
\]

The average duration of a hop is given by eq. (18a), whereas the average flight duration of all particles in-flight at a given time is given by eq. (18b). The average maximum height per hop is \( H/2 \), as was already determined in eq. (12), whereas the maximum height reached by the particles in flight at a given time is \( H \) (18c).

**Density profile.** To form the time-average of the density profile, the integration is over all velocities that are sufficiently high to reach a given height, i.e., \( v_z > \sqrt{2gz} \):

\[
\langle \rho \rangle = \int_{\sqrt{2gz}}^{\infty} \rho(z; v_z) P_M(v_z) \, dv_z = \frac{\pi}{4zH} \text{Erfc} \left( \sqrt{\frac{z}{H}} \right) \quad \text{(19)}
\]

where \( \text{Erfc} \) is the complementary Error function. This result has the correct normalization and average:

\[
\int_0^\infty \langle \rho \rangle \, dz = 1 \quad \text{(21a)}
\]

\[
\int_0^\infty z \langle \rho \rangle \, dz = \frac{H}{3} \quad \text{(21b)}
\]

The median height is determined numerically as \( z_m \approx 0.12H \).

For \( z \ll H \), eq. (20) takes the asymptotic form

\[
\langle \rho \rangle = \sqrt{\frac{4\pi}{Hz}} - \frac{1}{H} \quad \text{for} \quad z \ll H \quad \text{(22)}
\]

which implies that the density near the surface goes to infinity, as expected. In the opposite limit of large height,

\[
\langle \rho \rangle = \frac{1}{2z} e^{-z/H} \quad \text{for} \quad z \gg H \quad \text{(23)}
\]

The density decreases faster than exponential.

The time-averaged density profile is

\[
\langle \rho \rangle = \int_{\sqrt{2gz}}^{\infty} \rho(z; v_z) P_M(v_z) \frac{t_D}{\langle t_D \rangle} \, dv_z \quad \text{(24)}
\]

\[
= \frac{1}{2H} e^{-z/2H} K_0 \left( \frac{z}{2H} \right) \quad \text{(25)}
\]

where \( K_0 \) is the modified Bessel function of the second kind. The column integrals are

\[
\int_0^\infty \langle \rho \rangle \, dz = 1 \quad \text{(26a)}
\]

\[
\int_0^\infty z \langle \rho \rangle \, dz = \frac{2}{3} H \quad \text{(26b)}
\]

The median is determined numerically as \( z_m \approx 0.39H \).

For \( z < H \), \( K_0(z/2) = -\ln(z/4) - \gamma \), where \( \gamma \) is the Euler constant, and in this limit

\[
\langle \rho \rangle = -\frac{1}{2H} \left( \ln \left( \frac{z}{4H} \right) + \gamma \right) \quad \text{for} \quad z < H \quad \text{(27)}
\]

which implies that the density near the surface goes to infinity. In the opposite limit of large height, \( z \gg H \), \( K_0(z/2) = \sqrt{\pi/2} e^{-z/2} \), and therefore

\[
\langle \rho \rangle = \frac{1}{2} \sqrt{\frac{\pi}{z}} e^{-z/H} \quad \text{for} \quad z \gg H \quad \text{(28)}
\]

At large heights, the density falls off faster than an exponential.

Figure 1 compares \( \langle \rho \rangle \) and \( \langle \rho \rangle \) with the barometric law. What appears to be a “ground-hugging” population is actually part of a population described by a single temperature.

As apparent from eqs. (10a,10b), the near-surface divergence arises from particles with small vertical launch velocities. Typically these will have small launch angles.

**Armand distribution.** There is no compelling reason to assume the launch velocities of atoms and molecules desorbed from a surface are distributed according to Maxwell-Boltzmann (MB). That Maxwellian launch velocities from a solid surface do not result in a barometric exosphere has long been realized based on Monte-Carlo simulations (Smith et al. 1978; Hodges 1980), and it has been proposed that an anisotropic distribution of launch velocities, \( P(v_z) \propto v_z \exp(-s_A v_z^2) \), should be assumed. This is the so-called “Maxwell-Boltzmann flux” (MBF) or Armand distribution, which has a basis in desorption chemistry (Armand 1977), although the reason it was introduced is to achieve a barometric density profile. Because the surface is rough on small scales, the local surface normal rarely points in the direction of gravity,
so it is difficult to argue this would represent reality on the macroscale.

The Armand distribution is

\[ P_A(v_z) = 2\sqrt{\frac{s}{\pi}} v_z e^{-s A v_z^2} \quad \text{with} \quad s_A = \frac{m}{kT} = \frac{1}{gH} \]  

(29)

which has averages

\[ \langle v_z \rangle_A = \frac{1}{2} \sqrt{\frac{s}{s_A}} \quad \langle v_z^2 \rangle_A = \frac{1}{s_A} = \frac{kT}{m} \]  

(30)

\( s_A \) was chosen to achieve equipartition, \( m \langle v_z^2 \rangle_A / 2 = kT/2 \), although it is in the literature (Smith et al. 1978; Hodges 1980) defined as twice that value. The average of \( t_D \), using eqs. (3), (8), and (29), is

\[ \langle t_D \rangle_A = \frac{1}{g} \sqrt{\frac{s}{s_A}} = \frac{\sqrt{\pi H}}{g} \]  

(31)

The particle-averaged density profile is

\[ \langle \rho \rangle_A = \int_{-\infty}^{\infty} \rho(z; v_z) P_A(v_z) \, dv_z \]  

(32)

\[ = \frac{1}{H} e^{-z^2/H} K_0 \left( \frac{z}{H} \right) \]  

(33)

This density profile still diverges at the surface, although only logarithmically instead of \( \propto 1/\sqrt{z} \). The time average for particles in-flight is

\[ \langle \rho \rangle A = \int_{-\infty}^{\infty} \rho(z; v_z) P_A(v_z) \frac{t_D}{\langle t_D \rangle_A} \, dv_z \]  

(34)

\[ = \frac{2}{H} e^{-2z/H} \]  

(35)

This produces an exponential density profile, without divergence at the surface. The scale height is however half of that of the barometric formula (1). This is a consequence of allocating only \( kT/2 \) of energy into the vertical component. The MBF distribution traditionally reuses the exponential factor of the MB distribution and therefore implicitly allocates \( kT \) for the vertical mode. Whether the scale height is \( H \) or \( H/2 \) corresponds to a factor of two in inferred absolute temperature (2).

It is proposed here that the near-surface divergence corresponds to reality and the barometric law of the exosphere, as well as it may work for an exobase, ought to be abundant for the surface-bounded case.

3. COMPARISON WITH MEASUREMENTS

Measurements of the vertical density profile of atomic H and He are available from the UV spectrometers on the Mariner 10 mission to Mercury (Shemansky & Broadfoot 1977). Atomic hydrogen is expected to react with the surface or escape immediately, and hence the applicable theoretical expression is (20) and not (25). The data points reproduced from a plot in Shemansky & Broadfoot (1977) are shown in Figure 2. These, and other, authors interpret the observed profile in terms of two populations of different temperature. Equation (20) (green line) provides a dramatically better description of the data than the blue (exponential) lines, and makes it unnecessary to assume two populations. The measurements are consistent with a single population, at a single temperature that matches the surface temperature. (The data at about 200 km are a separate phenomenon not described by either theory.)

Unlike many other numerical models (e.g., Leblanc & Chaufray 2011), the model results of Wurz & Lammer (2003) reproduce the near-surface excess of H and He on Mercury.

Vertical profiles of Na and K have been measured for the Moon with Earth-based observations, and Sprague et al. (1992) describe them as two-component exospheres. These species are ejected at temperatures far above that of the surface, and theoretical expressions for constant \( g \) are not adequate to describe them. Nevertheless, the behavior of the near-surface density profile predicted by the theory for constant \( g \) may as well capture that for radially decaying \( g \), and potentially provides a simpler explanation for these observations.

4. CONCLUSIONS

The vertical density profile of a stationary thermal surface-bounded exosphere in a uniform gravity field, with a constant number of particles and a Maxwell distribution for launch velocities is given by eq. (25). The density approaches infinity near the surface and decays faster than exponentially at great height. For particles that only undergo a single or no hop, eq. (20) is appli-
cable, which exhibits an even stronger divergence at the surface.

These exact solutions are inconsistent with the barometric law, and may explain observed density profiles that have been interpreted as two-component exospheres in terms of a single component. Only probability distributions with a strong bias against relatively small vertical launch velocities do not create a ground-hugging population (10), and, in all cases, equipartition during vapor-solid contact results in a scale-height (14) significantly smaller than $H$ (2).

More broadly, these results imply that the theory of surface-bounded exospheres is insufficiently developed. In addition to thermodynamic solutions, the lateral transport properties, both in statistical and continuum form (Schorhöfer 2015), would be of considerable interest.

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