

# The Maxwell-Boltzmann velocity distribution and other limiting conditions at the boundary of a gas vapor

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Atomic or molecular thermal gas remain widely an attractive topic because of an extraordinary simplicity and reproducibility, along with convenient resonances easily addressed -in the optical region- with lasers. A current limit, notably for numerous linear techniques, is in the Doppler broadening. Selecting an atomic velocity is often a solution but the lab frame becomes a physical reality when the gas boundary has to be considered, implying limits to atom trajectories, and a (sudden) optical de-excitation. The redistribution on the wall is a delicate problem, as for an ideal Maxwell gas, ideal non interacting planar surfaces are assumed, implying an isotropic velocity distribution. Actually, at an atomic scale, there are no planar surfaces. Moreover, interactions are very important "on" the surface (physi- or chemi-sorption, partial spin de-excitation, ...). This implies that the "cos  $\theta$ " law of the flux of departing atoms is questionable. Until now, a dedicated experimental set-up [1], has not enabled us to point deviations from the Maxwell-Boltzmann velocity distribution, but has already allowed to probe the distribution of very grazing incidences (up to 88.5° from the normal), despite obvious technical limitations of a too elementary set-up could.

Aside from revisiting this old question of the boundary of a gas, various effects associated with surfaces are currently considered. More in the "long-range", the van der Waals atom-surface interaction exceeds the thermal energy for relatively large distances (~1 nm). This means that assuming a "thermal" distribution of kinetic energy for atoms "just" does not lead to a similar thermal distribution at a distance from the surface, leading us to suggest that there could be some kind of a trapping region [2]. Through the thermal emissivity of a surface in specific surface modes [3, 4], possibly in resonance with atomic transitions [5], one may conceive that a vapor (notably for molecular vibration) does not respect thermal distribution of internal energy, because the vapor is not truly "isolated" from the surface. These considerations about surfaces are naturally important when the trend is to confine an atomic or molecular vapor, as it can be done within the interstices of an opal [6], or in a porous medium [7], where even Rydberg levels can be studied. At last, for a well-tuned nanostructured ZrO<sub>2</sub> boundary in air, irradiation can induce a localized O<sub>2</sub> dissociation through a nanostructuring of the electromagnetic-field, so that the boundary itself is smoothly reshaped by a nano-etching governed by the magnetic component of the irradiating light.

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