

Evaporation for review—and with it global warming

October 22 2015



Recoil of evaporating molecules changes the pressure at the surface of the liquid. Credit: IPC PAS, Grzegorz Krzyzewski

The process of evaporation, one of the most widespread on our planet, takes place differently than we once thought - this has been shown by new computer simulations carried out at the Institute of Physical Chemistry of the Polish Academy of Sciences in Warsaw. The discovery has far-reaching consequences for, among others, current global climate models, where a key role is played by evaporation of the oceans.



They all evaporate: oceans and seas, microdroplets of fuel in engines and the sweat on our own skin. For every one of us <u>evaporation</u> is of paramount importance: it shapes the climate of the planet, it affects the cost of car travel, and is one of the most important factors controlling the temperature of the human body. So common is it that it seemed that evaporation was a phenomenon that had been stripped of any more secrets. In the renowned scientific journal *Soft Matter* physicists from the Institute of Physical Chemistry of the Polish Academy of Sciences (IPC PAS) in Warsaw, Poland, prove that this belief was erroneous and the mechanism of evaporation must operate differently than had previously been assumed.

"Science copes badly with descriptions of processes occurring in nature. We are perfectly able to describe the states at the beginning of the process and at its end. But what happens in between? How does the given process really take place? For so many years we have been asking ourselves this question in relation to the phenomenon of evaporation - and we are coming to ever more interesting conclusions," says Prof. Robert Holyst (IPC PAS).

In scientific and technical deliberations we use the Hertz-Knudsen equation, known for over a hundred years, to describe the <u>evaporation</u> <u>rate</u>. What follows from it is quite an intuitive prediction: that at a given temperature the rate of evaporation of the <u>liquid</u> depends on how different the actual pressure at the surface is from the pressure which would be present if the evaporating liquid were to be in thermodynamic equilibrium with its environment.

"The further the system is from equilibrium, the more dynamically it should return to it. It's so intuitive! So we checked the Hertz-Knudsen equation - because we like to check. In order to do this we prepared exceptionally accurate computer simulations which allowed us for the first time to take a closer look at the process of evaporation," explains



Dr. Marek Litniewski (IPC PAS).

Advanced computer simulations carried out using molecular dynamics showed that the values of some parameters describing evaporation are even several times larger than those predicted by the Hertz-Knudsen equation. However, an even more interesting effect was noted: the stream of gas being liberated from the surface of the liquid during evaporation changed very little despite significant fluctuations in pressure.

"There could only be one conclusion from this observation: the rate of evaporation and the vapour pressure, that is, the physical quantities that were previously considered to be closely related, were not so. For more than a century we had all been making a serious error in the theoretical description of the phenomenon of evaporation!," says Dr. Litniewski.

The hitherto model of evaporation was based on the principle of conservation of mass: the mass of molecules released from the surface of a liquid had to respectively increase the mass of the gas in its surroundings. Physicists from the IPC PAS noticed, however, that since the particles released from the surface have a certain velocity, in order to describe this phenomenon what should be applied is the principle of conservation of momentum.

"We realized that to some extent evaporation resembles shooting from a cannon: the missile flies in one direction, but the overall momentum of the system must be maintained, so the gun recoils in the opposite direction. The same happens with the molecules of evaporating liquid. Since there is an increase in momentum, there must be recoil, and if there is recoil, the pressure felt by the molecules on the surface of the liquid will be different," says Prof. Holyst.

The new computer simulations were also used to measure the velocities



of the molecules released from the liquid surface. They proved to be small, of the order of hundreds of micrometres per second, which corresponds to only a few kilometres per hour. This fact means that practically any naturally occurring flow over the surface of the liquid has to strongly interfere with the evaporation process. The evaporation cannot thus be described by an equation derived for a very specific case, for liquid that is in thermodynamic equilibrium with the environment.

The discovery of the IPC PAS researchers is of the utmost importance for, among others, the understanding of the real mechanisms responsible for global warming. Contrary to common belief, the most abundant greenhouse gas in the atmosphere of our planet is not carbon dioxide but water vapour. At the same time, it is known that the speed of flow of air masses over the oceans can significantly exceed one hundred kilometres per hour and therefore they will certainly affect the rate of evaporation. The hitherto evaluation of the rate of evaporation of the oceans must therefore be subject to error, which will certainly affect the accuracy of the predictions of contemporary models of the Earth's climate.

Provided by Polish Academy of Sciences

Citation: Evaporation for review—and with it global warming (2015, October 22) retrieved 7 May 2024 from https://phys.org/news/2015-10-evaporation-reviewand-global.html

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