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VIEWPOINT

Standardizing the Thermodynamic Definition of Daytime Subambient Radiative Cooling

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Daytime and nighttime radiative cooling has emerged as a highly promising and versatile technology with broad applications across various sectors, including building energy management, renewable energy systems, and environmental sustainability.[1−11] Grounded in the principles of radiative heat transfer, radiative cooling harnesses the natural heat exchange between an emitter and the frigid expanse of the universe to reduce the emitter surface temperatures lower than the surrounding ambience with proper optical property and thermal insulation. As the second law of thermodynamics dictates, transferring heat from the colder indoor space to a hotter outdoor ambience requires external work input. Nonetheless, in the case of radiative cooling, the extremely low temperature of deep space (4 K) functions as an inherent heat sink via thermal radiation, eliminating the need for extra work. To unlock the potential of this promising cooling mechanism, materials must optimize their thermal emissivity within the atmospheric transparent window while concurrently minimizing solar absorptivity. Given that subambient radiative cooling transcends the conventional bounds of terrestrial heat flow, its quantification demands meticulous adherence to rigorous and standardized procedures. We contend that a comprehensive elucidation of the fundamental thermodynamic principles and definitions governing subambient radiative cooling is of utmost importance. This *Viewpoint* aims to establish standardized protocols for both experimental measurements and theoretical simulations, facilitating the development of this prolific research field.

A thorough thermodynamic analysis of heat transfer, conducted within a precisely defined control volume, is crucial for comprehending the fundamental distinctions between daytime passive subambient radiative cooling and its counterparts. An improperly defined control volume can result in an inaccurate ambient temperature, creating confusion in delineating the concept of subambient radiative cooling. By performing the energy balance analysis in the control volume of the cooling unit, the radiative cooling power can be qualitatively described as eq 1:

$$P_{cool} = P_{rad} - P_{sun} - P_{amb} - P_{conv+cond} \quad (1)$$

where P_{cool} is the net cooling power, P_{rad} is the emitted radiative heat flow, P_{sun} is the solar heat gain of the emitter, P_{amb} is the inward thermal radiation from the atmosphere, and $P_{conv+cond}$ is the parasitic heat due to convection and conduction. A detailed explanation of these terms (wavelength and angle dependence) is provided in the Supplementary Note 1. Illustrated in Figure 1A, for an object (emitter) that exhibits a high thermal emissivity but only a moderate solar reflectivity, the equilibrium temperature upon sunlight exposure is higher than the ambient temperature due to excessive solar heating (P_{sun}), as we normally expect for ordinary objects. On the other hand, a subambient radiative cooling can greatly reduce P_{sun}, causing its temperature to be lower than ambient, hence bringing great potential for mitigating the energy demand for cooling in the ever-increasing global temperature. It is important to note that although we represent the deep universe cooling source with 3K, the actual inward thermal radiation from the sky/atmosphere occurs at a significantly higher temperature, known as the ambient temperature, and the power of radiation varies with wavelength. (Supplementary Note 1) Even within the transparent window (8−13 μm), the atmosphere is not entirely transparent, typically exhibiting 70−90% transparency. Consequently, the nontransparent portion of the atmosphere emits thermal radiation back to the emitter, denoted as P_{amb} in eq 1. It is crucial to account for this factor when discussing the thermodynamics of radiative cooling.

The key question (and the cause of confusion) is − *what is the definition of "ambient temperature"*? If we define it as "the temperature of the immediate environmental surroundings", then the choice of "surroundings" needs to be clear and universal rather than arbitrary. First, because radiative cooling requires direct access to the sky, we should explicitly define it as "ambient air temperature" with two important criteria: **(i)** It should only depend on the weather conditions rather than the individual measurement equipment. For example, the U.S. Climate Reference Network (USCRN) has climate monitoring stations around the U.S., all following a rigorous protocol to measure the air temperature.[12] Such weather stations are equipped with a radiation shield to ensure unobstructed air circulation and prevent direct solar influence.[13] **(ii)** The ambient air should be treated as an infinite heat sink. This is the same as the bulk fluid temperature, T_∞, in a classical external flow heat transfer analysis in any refrigerator. From the thermodynamic perspective, if the ambient air is the coldest

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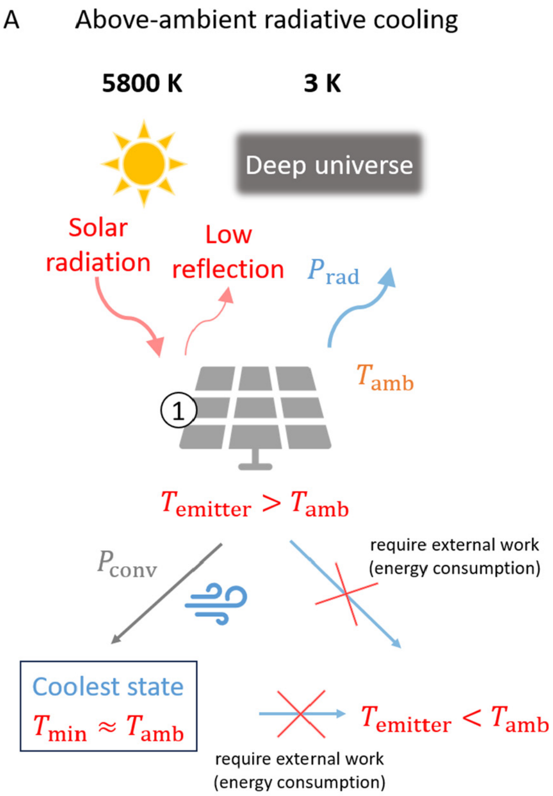

Figure 1. Thermodynamic analysis for above-ambient (A) and subambient (B) radiative cooling. Note the values of emitter and ambient temperatures are for qualitative comparison only.

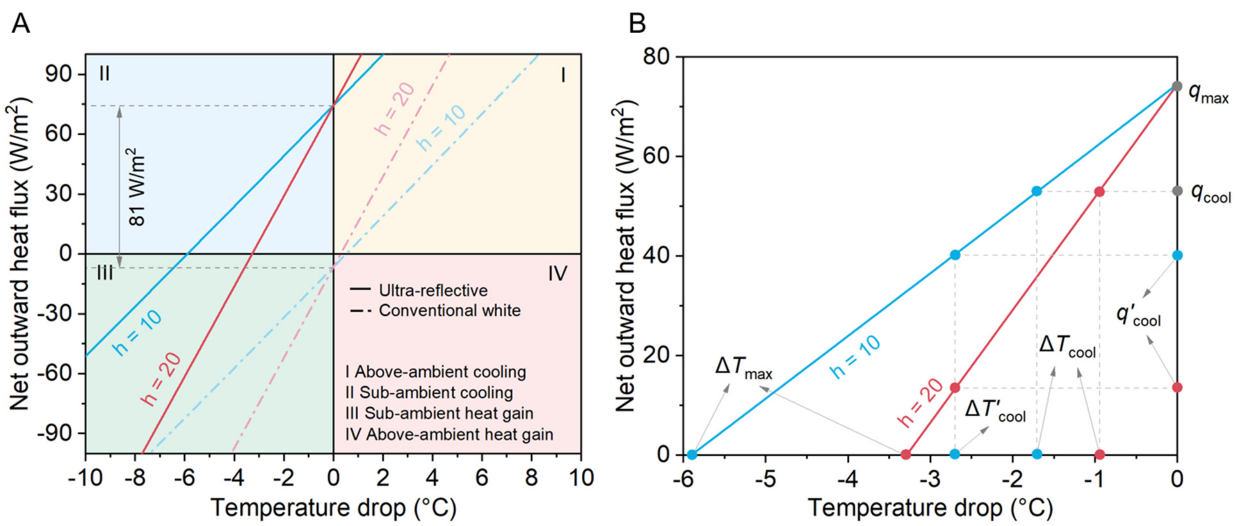

Figure 2. Theoretical calculation of the net outward heat flux (cooling power) as a function of temperature drop, where the temperature drop is defined as $T_{emitter} - T_{amb}$.

heat sink, then ambient air temperature is also the lowest temperature possible without work input (assuming there is no latent heat cooling involved). Strong convection can enhance the cooling power, moving heat from the radiative cooler to the ambient air, but any subambient thermal condition would be impossible without external work. Erroneous choice of control volume will lead to a different definition of "ambient air temperature", as we will elaborated upon in the subsequent sections of this paper.

On the other hand, true daytime passive subambient temperature can be realized when the emitter simultaneously possesses a sufficiently high solar reflectivity and thermal emissivity. (Figure 1B) This configuration enables the emitter to radiate its heat into deep space and block the solar radiation. This approach introduces the three-kelvin-cold universe as a second heat sink much colder than the ambient air, so it can achieve subambient cooling without external work and still entirely comply with the second law of thermodynamics.

The discussion on thermodynamics above pointed out the critical difference between above- and subambient radiative coolers—only the latter can remove heat from a low-temperature indoor space without work input. Recently, a few instances have confused ambient temperature with *"enclosure air temperature"*. Such enclosure air temperature cannot be treated as an infinite heat sink, and it strongly depends on the enclosure's optical and thermal properties. As a result, it is common to observe an enclosure air temperature as high as 40−50 °C. This high temperature is unrealistic, and it becomes trivial for an emitter to achieve a lower temperature because it simply needs to have a slightly higher solar reflectivity than the enclosure interior. This kind of emitter is by no means "subambient". We are fully supportive of more research efforts in radiative cooling materials development, but we recommend that these materials should be properly regarded as "cooler than the object in comparison", in which the object can be the enclosure itself, commercial white paint, or any control samples.

The foremost challenge in realizing subambient radiative cooling is achieving high solar reflectivity, a feat beyond the reach of many conventional materials. Neglecting this crucial aspect exposes the emitter to excessive solar heat gain, compromising the net cooling power. As an example to numerically demonstrate the differences, Figure 2A shows a detailed computation of radiative heat transfer for two emitters under an incident solar radiation of 900 W/m^2: an ultrareflective emitter (α_{solar} = 0.03, ε_{IR} = 0.98) and a conventional white emitter (α_{solar} = 0.12, ε_{IR} = 0.98). α_{solar} and ε_{IR} mean solar absorptivity and IR thermal emissivity, respectively. The conventional white emitter absorbs excessive solar radiation and fails to sustain a positive net outward heat flux at a subambient temperature. For this conventional emitter, positive cooling power is only attainable when the temperature of the emitter exceeds that of the ambient surroundings (the first quadrant). Stronger convection (h = 20 W/m^{2}K) can enhance the cooling power at the same temperature drop, but it cannot move the curves to the second quadrant, thereby precluding the achievement of subambient cooling. In contrast, for the ultrareflective emitter, the high solar reflectivity of 0.97 greatly reduces the solar heat gain and moves both curves up along the y-axis, entering the subambient cooling quadrant. It is important to underscore that, in this case, excessive convection decreases the net outward heat flux (cooling power) and the maximal temperature drop. It is also worth noting that the vertical distance between the curves of ultrareflective and conventional white emitter is exactly the difference in their solar heat gain (900 × (0.12−0.03) = 81 W/m^2). This means, at zero convective/conduction influence, the inward heat gain of ultrareflective emitter is 81 W/m^2 less than that of the conventional white emitter.

We further discuss the working condition of a subambient radiative cooler and the influence from convective/conductive loss in Figure 2B. The intercepts on the x-axis are the theoretical maximum temperature drop ΔT_{max} that the ultrareflective emitter can achieve. This can only be achieved when the emitter is in an open-circuit configuration without any usable cooling power. All the radiative cooling potential is counteracted by the parasitic heat flow to the emitter. On the other hand, the maximum available cooling power q_{max} is achieved in the short-circuit condition when the convective/conductive heat loss and the temperature drop are zero, which is the intercept on the y-axis. In reality, the working condition of this subambient radiative cooler should operate along this line with the corresponding temperature drop, ΔT_{cool} and available cooling power, q_{cool}, which depends on the heat transfer substance used to deliver the cooling power to the objects (e.g., buildings and human body). Under the same cooling power q_{cool}, the radiative cooler under lower convection (h = 10 W/m^{2}K) can reach a larger temperature drop ΔT_{cool}. Similarly, under the same temperature drop $\Delta T'_{cool}$, the radiative cooler under lower convection offers a higher cooling power q'_{cool}. Having a lower parasitic heat transfer coefficient (h = 10 W/m^{2}K) means the subambient radiative cooler has a larger range of working conditions with the same q_{max} that is determined only by the optical properties.

Given the strong impact of the surrounding weather conditions, the outdoor measurement of radiative cooling needs to be carefully designed to accurately assess the cooling potential (see detailed discussion in Supplementary Note 2). Since subambient cooling is thermodynamically different from above-ambient cooling, the ambient temperature should be measured based on rigorous protocols established by weather meteorologists rather than arbitrary definitions. The weather station equipped with a radiation shield is widely recognized as a standard method for measuring ambient temperature, which typically consists of a cylindrical or spherical enclosure that envelops the thermocouple. Constructed from materials such as painted aluminum or silver mylar, chosen for their capacity to reflect solar radiation and effectively dissipate heat, the shield's design facilitates airflow around the sensors while shielding them from direct sunlight and other sources of radiant heat. Additionally, the well-insulated and guard-heater-enabled thermal design improves the accuracy of the temperature drop and cooling power by suppressing parasitic heat loss. A checklist for ensuring the accuracy of heat transfer measurement apparatus is provided in Supplementary Table S1. Theoretical study based on the local weather conditions (humidity and cloud cover fraction) and numerical building energy saving modeling provides a more comprehensive analysis of the outdoor daytime radiative cooling potential. Additionally, the precise definition of the control volume when analyzing the energy balance in heat transfer measurements is crucial, as discussed in Supplementary Note 2. Nevertheless, the season and weather dependence of the radiative cooling measurement can be problematic for accelerating the research. Recently, several indoor measurement setups have been demonstrated, utilizing liquid nitrogen to emulate the cold deep universe, coupled with a solar simulator to provide consistent sunlight levels.[14,15] This approach eliminates the influence of outdoor weather conditions, ensuring a stable and controllable outcome. In addition, obtaining the azimuthal angle-resolved solar absorptivity and thermal emissivity spectra can improve the predictability of heat transfer modeling software for various solar radiation, atmosphere window, and even territorial objects. These lab-setting and digital twin approaches can also facilitate scientific communication, leading to a robust and unifying research community that continues to push the boundary of radiative cooling.

Additional discussion and references on control volume and heat transfer measurement are provided in the Supporting Information.

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■ ASSOCIATED CONTENT

Supporting Information

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Additional discussion and references on control volume and heat transfer measurement, in Supplementary Notes 1 and 2 and Supplementary Table S1 (PDF)

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Notes

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The authors declare no competing financial interest.

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