What is Atmospheric Temperature?

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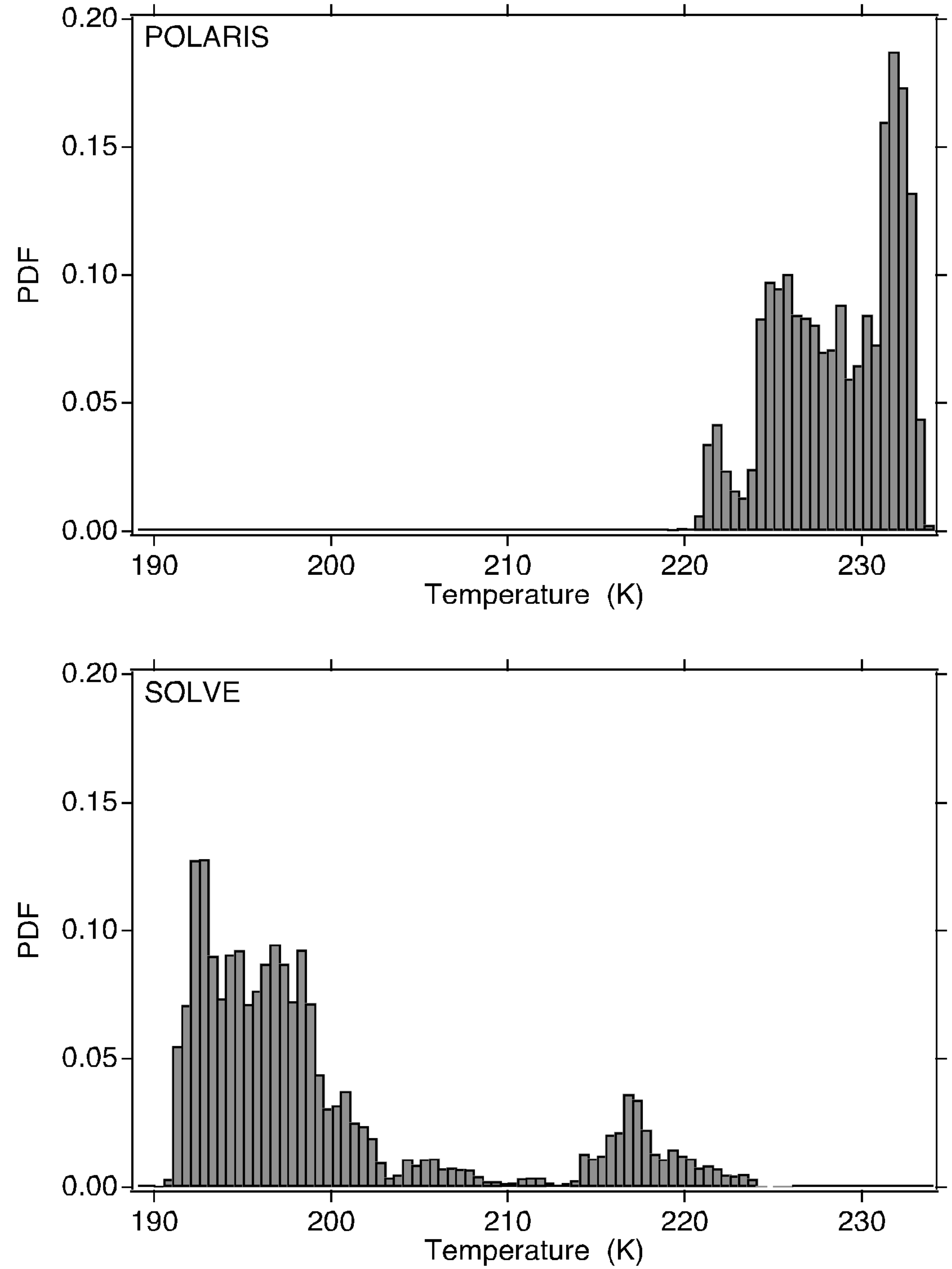
Molecular velocity distributions and generalized scale invariance in the turbulent atmosphere, *Faraday Discussions*, **130**, 181 - 193, doi: 10.1039/b410551f, [2005].

Temperature PDFs in the Arctic

Airborne observations of ozone, temperature and the spectral actinic photon flux for ozone in the Arctic lower stratosphere April-September 1997 and January-March 2000 allow a connection to be made between the rate of production of translationally hot atoms and molecules via ozone photodissociation and the intermittency of temperature. Seen in the context of non-equilibrium statistical mechanics literature results from molecular dynamics simulations, the observed correlation between the molecular scale production of translationally hot atoms and molecules and the macroscopic fluid mechanical intermittency of temperature may imply a departure from Maxwell-Boltzmann distributions of molecular velocities, with consequences for chemistry, radiative line shapes and turbulence in the atmosphere, arising from over-populated high velocity tails of the probability distribution functions (PDFs).

The figures to the right show PDFs of 5 Hz temperature (approximately 40 m resolution) for 'horizontal' flight legs from the POLARIS and SOLVE ER-2 experiments. Note the warm most probable value in the summer anticyclone and the fat tail of cooler values, with a cold most probable value in the winter vortex accompanied by a fat tail of warmer values. The asymmetric, fat-tailed PDFs are an adjunct of multifractal behavior.



Scaling

Here we use the quantity H_1 to denote the scaling exponent calculated from a data series f(t) by application of the first order structure function. The q_{th} order structure function of f(t) is defined by

$$S_q(r;f) = \langle|f(t+r) - f(t)|_q\rangle$$

where the lag r is real and positive, the angle brackets denote an average over t and ensemble averaging over f. We denote by $\zeta(q)$ the functional relationship of $\log S_q(r;f)$ to $\log(r)$ and implicitly define the constant H by

$$\zeta(q) = qH - K(q)$$

where K(q) is an intermittency correction (frame 3). It turns out that for conservative multifractals such as we are dealing with here, $K(1) = 0$, leading to a particularly simple expression for H as $\zeta(1)$. In fact, even for $q = 2$, K(q) is not very large, so it is possible to write $H \approx \zeta(2)/2$.

The quantity H is called a scaling exponent because when $\zeta(q)$ is linear it follows that

$$\langle|\Delta f(\Delta t)|_q\rangle \approx (\Delta t)_{\zeta(q)}.$$

Similarly the spectral exponent β indicates that an energy spectrum is in power law relationship with its wave numbers:

$$E(\omega) \approx \omega_{-\beta}$$

ζ, β and H are related by

$$\beta = 1 + \zeta(2) \approx 1+2H.$$

Intermittency

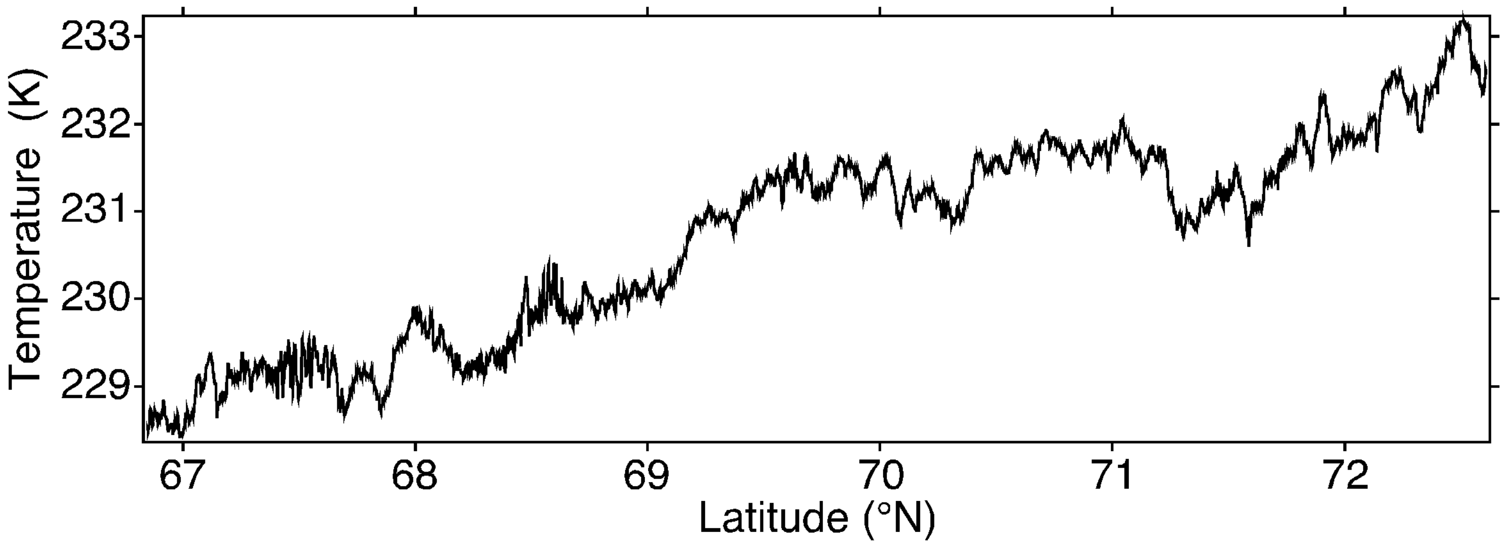
Because $K(1) = 0$, the quantity H_1 is a good estimate of the scaling exponent in both monofractal and multifractal cases. The exponent C_1 measures the intermittency of the signal and takes on values from zero to unity. Values near zero characterize a signal with low intermittency, for example a Brownian motion, and values near unity characterize a signal which is highly intermittent, for example a Dirac δ-function. Values in the range 0.02 to 0.10 seem to characterize atmospheric quantities, and although they are small, they are significant. Considering the signal $f(t)$ to have been observed at discrete time intervals $t = 1, 2, 3, \ldots, t_{max}$, define

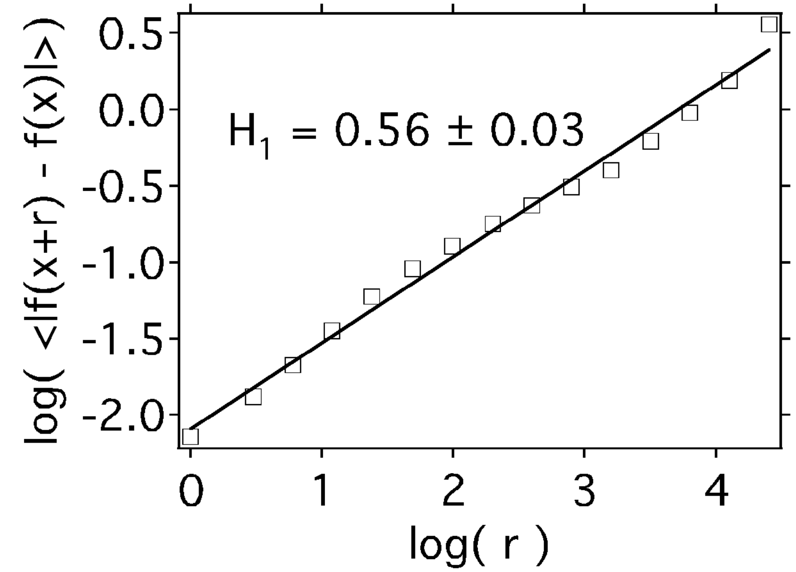
$$\varepsilon(1,t) = \frac{|f(t+1) - f(t)|}{\langle |f(t+1) - f(t)| \rangle}, \quad t = 1, 2, 3, \ldots t_{max}$$

$$\varepsilon(r,t) = \frac{1}{r} \sum_{j=t}^{t+r-1} \varepsilon(1,j), \quad t = 1, 2, 3, \ldots t_{max} - r$$

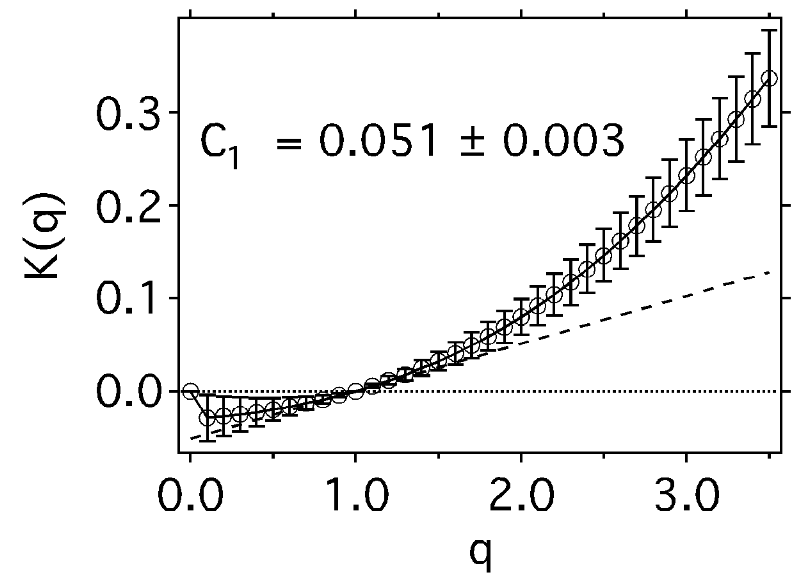
For our signals, it is found that the quantity $\langle \varepsilon(r,t)^q \rangle$ has a power law dependence on the scale r. An unweighted linear least squares fit to $\log\langle \varepsilon(r,t)^q \rangle$ versus $\log r$ provides a slope $-K(q)$. A plot of $K(q)$ versus q shows a convex function with $K(0) = K(1) = 0$. The exponent C_1 is defined as $K'(1)$, evaluated here numerically from the slope defined by the points $(0.9, K(0.9))$ and $(1.1, K(1.1))$. The uncertainty estimate in C_1 is obtained by taking the square root of the sum of the squares of the 95% confidence intervals returned by the unweighted linear least squares fits corresponding to $q = 0.9$ and $q = 1.1$.

19970506 - 5 Hz Data





Sample calculation of H_1 and intermittency C_1 for a POLARIS flight leg. Note that $H_1 = 5/9$.



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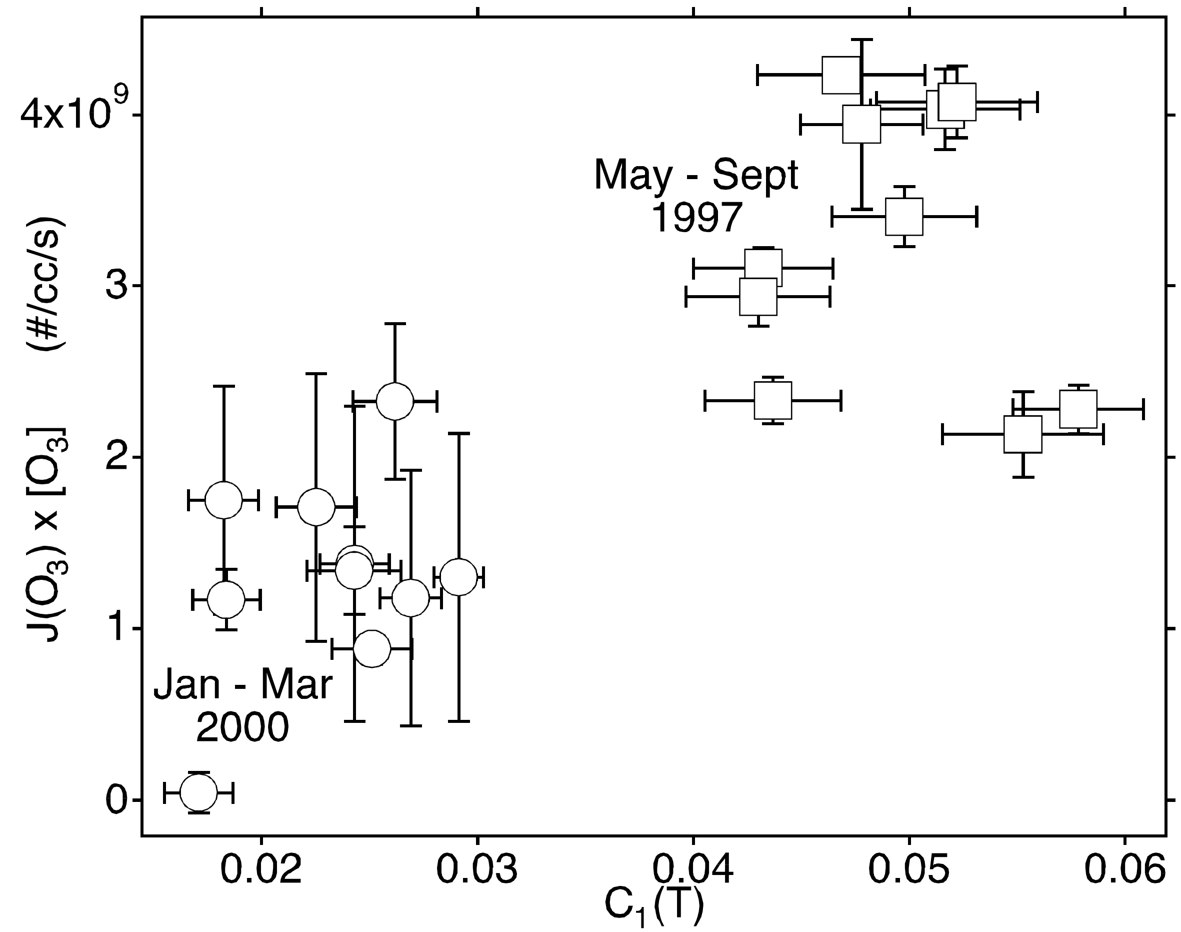
Ozone Photodissociation Rate vs. Intermittency of Temperature

Ozone photodissociation rate averaged over horizontal legs plotted against the intermittency of temperature for the same flight leg. The intermittency of temperature is correlated only with $J[O_3]$ and temperature itself (next frame). There is no correlation with either J or $[O_3]$ alone, or with other scaling exponents. J was calculated from observations of the spectrally resolved solar actinic flux and overhead ozone column.



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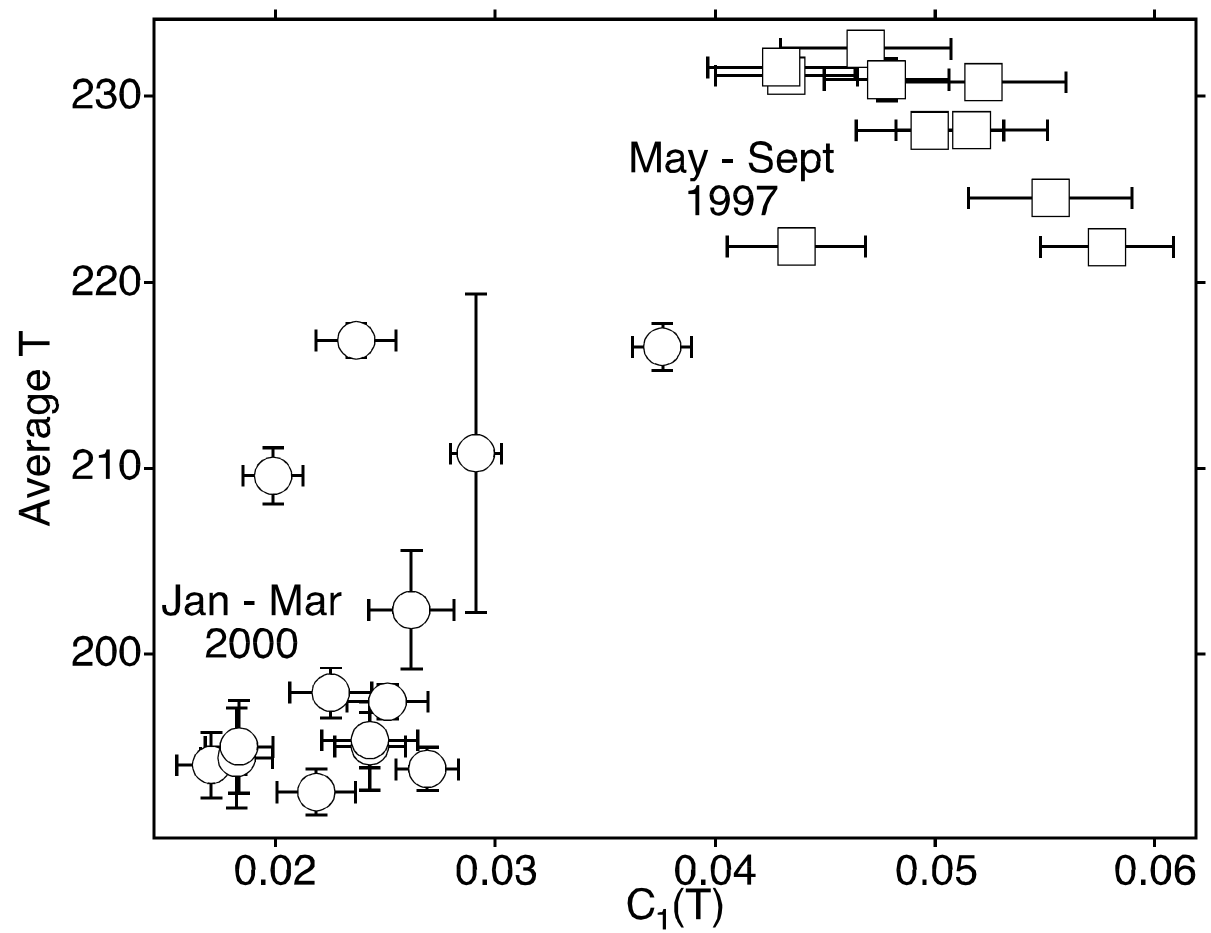
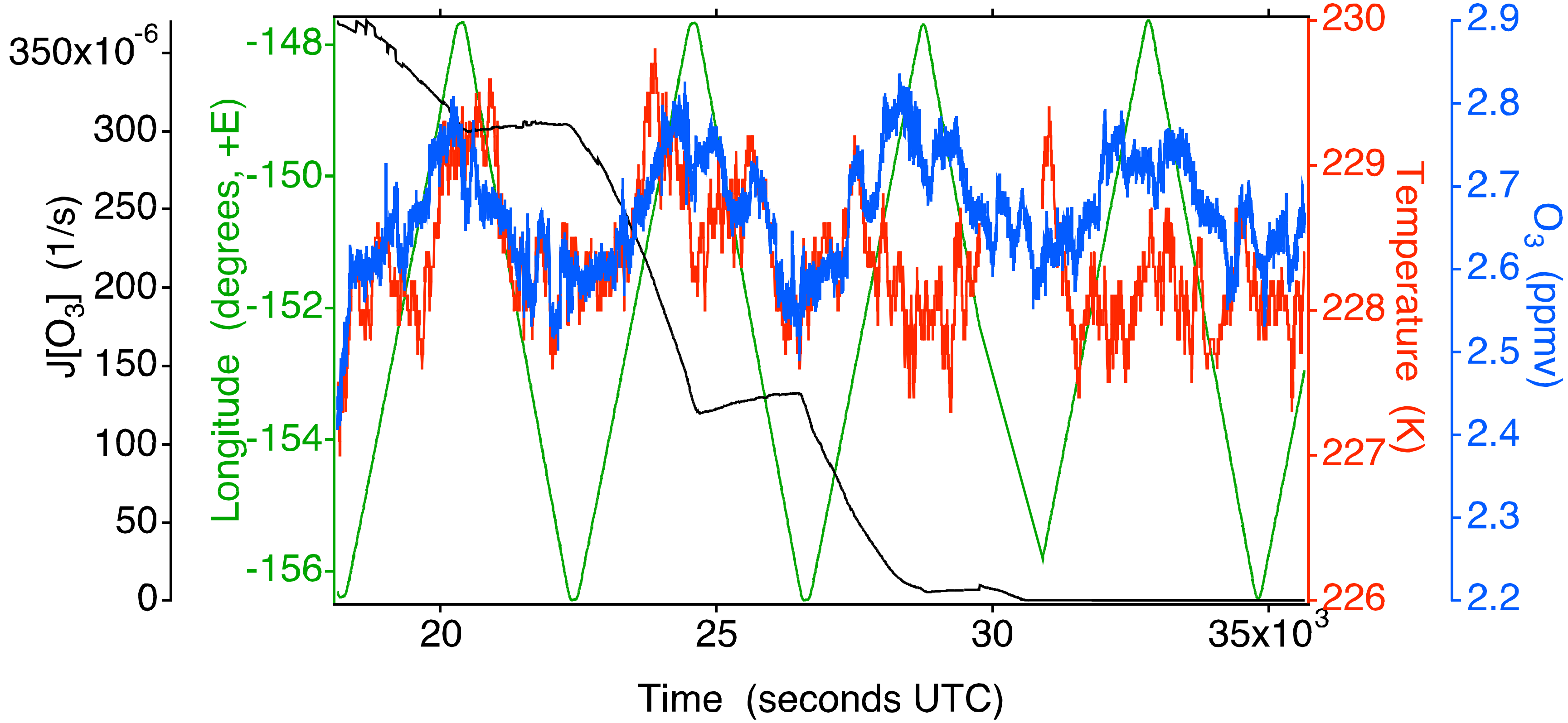
• E C Richard, K C Aikin, A E Andrews, B C Daube Jr., C Gerbig, S C Wofsy, P A Romashkin, D F Hurst, E A Ray, F L Moore, J W Elkins, T Deshler and G C Toon, *Geophys. Res. Lett.*, **28**, 2197 (2001)

Average Temperature vs. Intermittency of Temperature



Temperature averaged over horizontal flight legs is correlated with the intermittency of temperature calculated for the same flight leg.

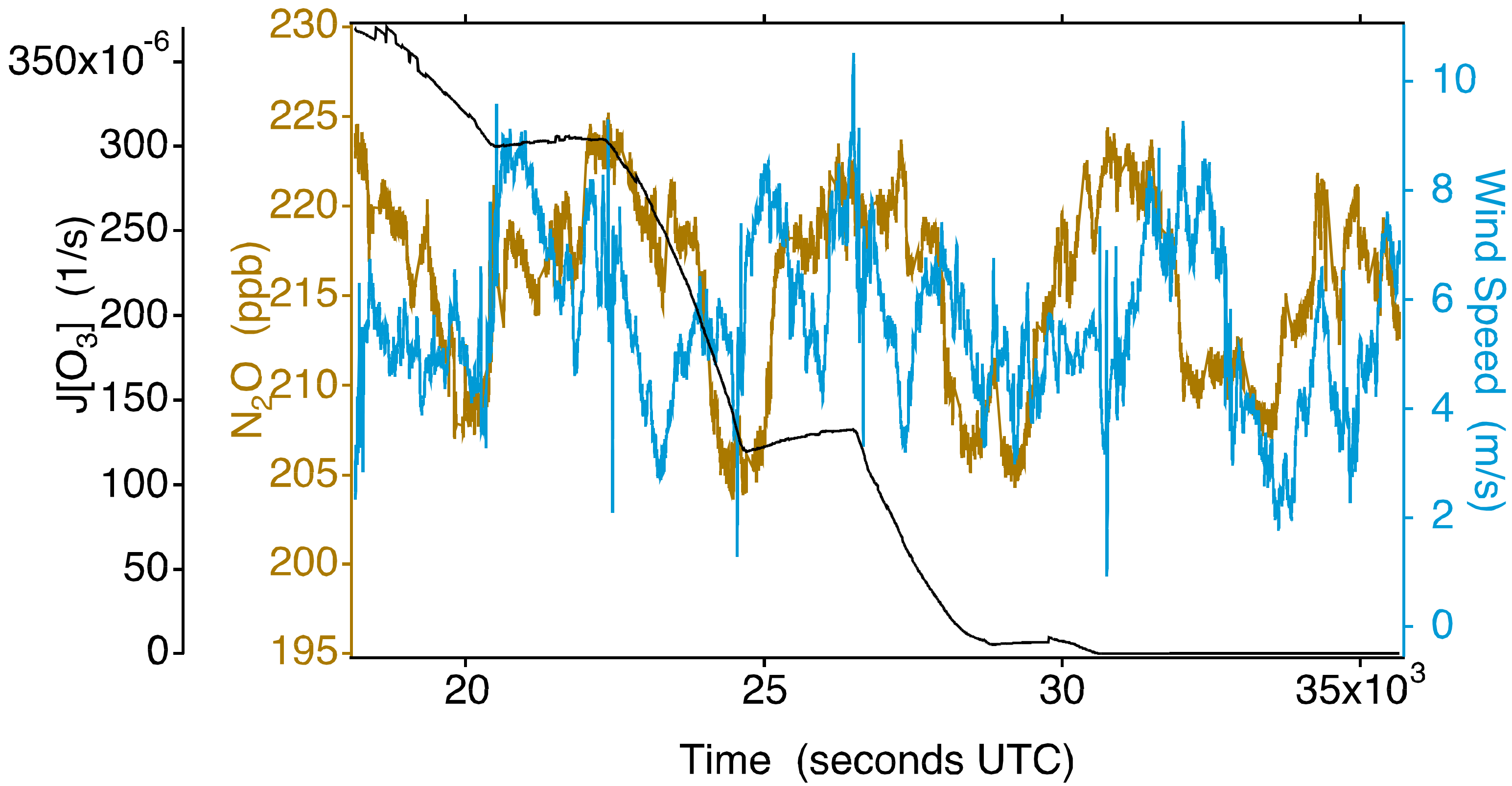
19970509 - 1 Hz Data



Flight data for 19970509, racetrack segments either side of the terminator at latitude 65°N. Longitude (green), $J[O_3]$ (black), ozone (dark blue) and temperature (red).

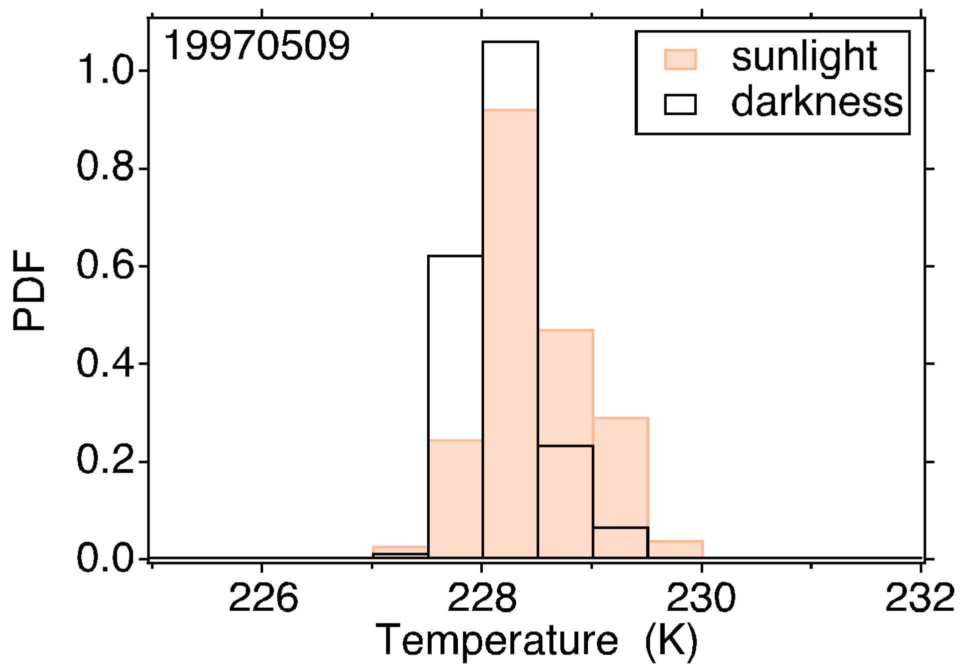
Note that while ozone is approximately symmetrical about $J[O_3] \approx 0$, temperature is not; it is warmer in the sunlit air. See also wind speed and nitrous oxide in next frame.

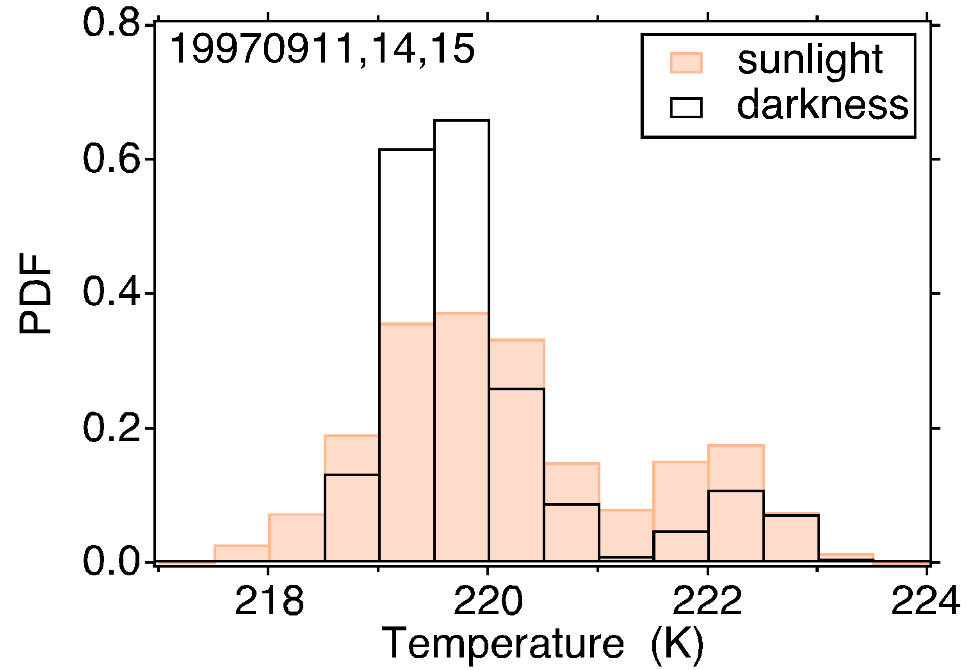
19970509 - 1 Hz Data



Same flight as frame 7. $J[O_3]$, black; wind speed (light blue); nitrous oxide (brown). Note that wind speed and nitrous oxide are approximately symmetrical about the terminator, like ozone but unlike temperature. The wind speed was from an average direction of 040; the air moved less than 3% of each flight leg between longitudes 148 and 156 W. These flights constitute a direct measure of radiative heating rate on the sunlit side of the terminator; it was ~0.4 K in 2 hours.

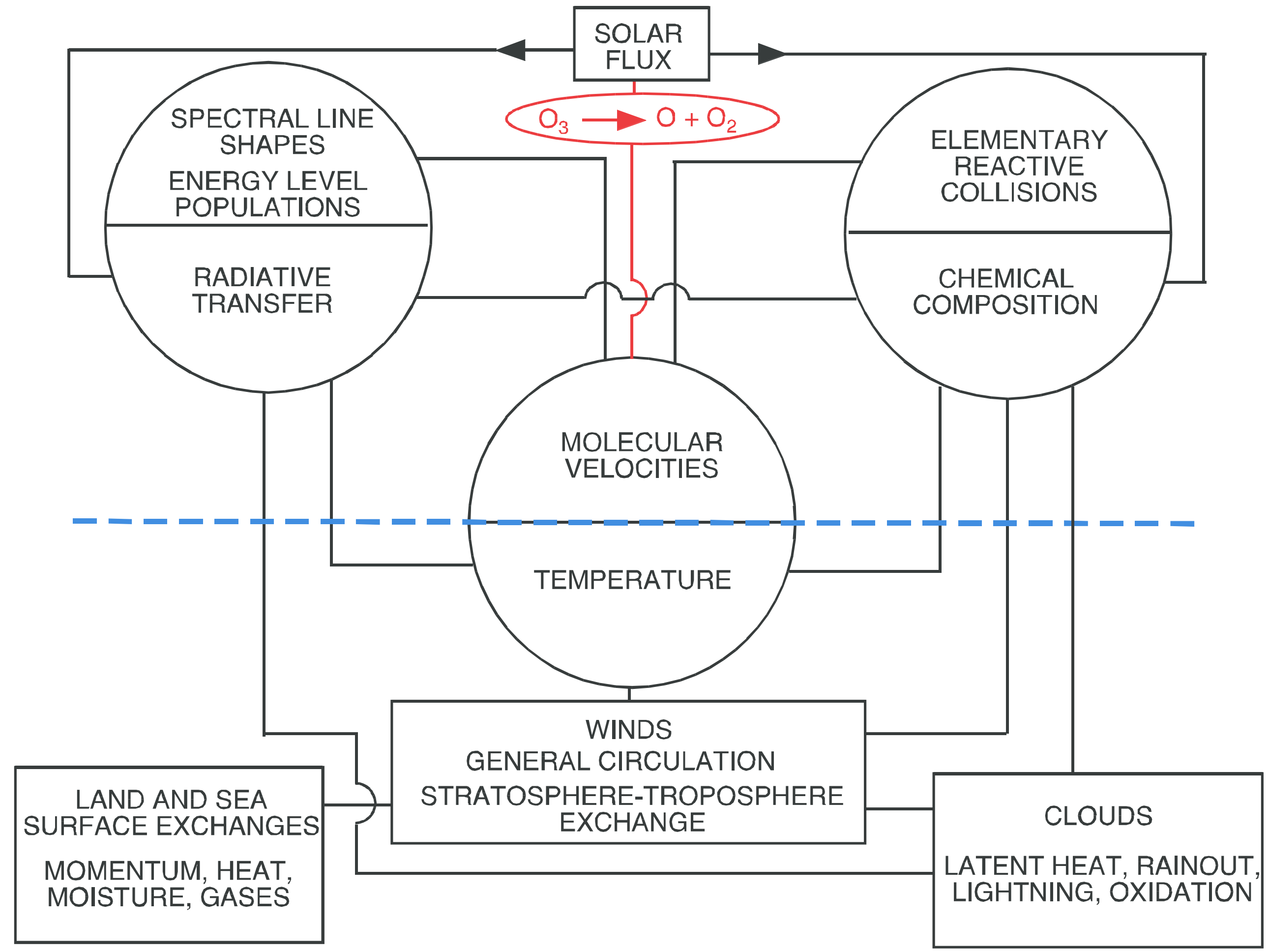
Sunlit and Dark Temperatures, Arctic Summer





PDFs of temperature for racetrack segments either side of the terminator, normalized to unity. Left, May; right, early September. Stippled areas represent sunlit data, clear areas represent dark data. Note that probability has moved from most probable values in the dark to warmer values in sunlight. See also previous two frames.

Connection: Molecular & Macroscopic Worlds



We have shown an observed correlation between the rate of production of translationally hot atoms and molecules from ozone photodissociation and the intermittency scaling exponent $C_1(T)$ of temperature from generalized scale invariance, using ER-2 observations in the Arctic lower stratosphere. Appeal to molecular dynamics literature simulations showing interactive generation of vortices (ring currents) by fast molecules on time scales of 10^{-12} s and space scales of 10^{-8} m offers a plausible mechanism for the correlation. The consequences of non-Maxwell-Boltzmann velocity distributions in the atmosphere would be manifold. Among them are systematic effects on rates of reaction, the possibility that tropospheric ozone increases have affected the infrared absorption properties of water vapour and carbon dioxide in the pressure-broadened line wings, and the possibility that the turbulent transfer of heat proceeds upscale by the ring current mechanism; diffusive formulations of transport would then be suspect on any scale from 10 nm to the earth's circumference. All these could be important as field observations become more accurate and tests of theory are at the tens of per cent level or better rather than factors of two or worse. Finally, although atmospheric temperature is well-defined and measurable, it may not correspond to an average over the distribution of molecular speeds associated with the Maxwell-Boltzmann function, with the consequence that it cannot be expressed simply in terms of the most probable, central velocity; during daylight, it may depend upon the ozone abundance and moreover could be different for the troposphere and stratosphere.

Temperature

Definition

The absolute temperature, T, of a system is the reciprocal of the derivative of the entropy, S, with respect to its energy, E:

$$\frac{dS}{dE} = \frac{1}{k_B T}$$

[Landau & Lifshitz, *Statistical Physics*, *Course of Theoretical Physics*, Vol. 5, 3rd ed., Chapters 1 - 3; k_B is Boltzmann's constant.]

T is purely statistical, having strict meaning only for macroscopic bodies at equilibrium. One can, of course, observe with a calibrated thermometer. It averages over the velocity distribution of the molecules impinging on it.

Microscopic View

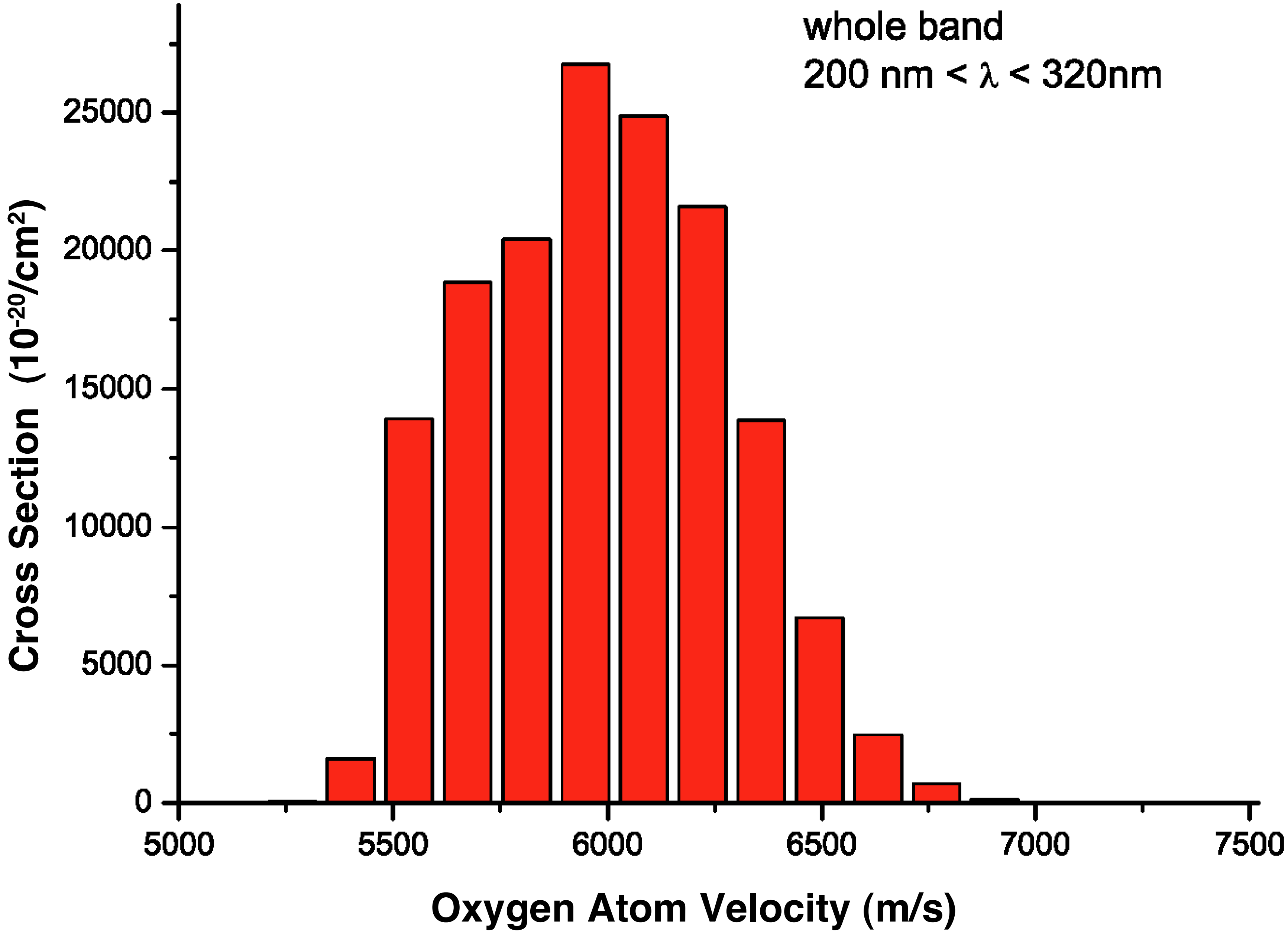
The total kinetic energy of N classical particles is $3NT/2$.

In terms of distributions of molecular velocity component v_x

$$\overline{v_x^2} = \sqrt{\frac{m}{2\pi k_B T}} \int_{-\infty}^{\infty} v_x^2 e^{-mv_x^2/2k_B T} dv_x = \frac{k_B T}{m}$$

In three dimensions, $T \propto \overline{v^2}$.

Velocity Distribution of O(^{1}D) Atoms



Velocity distribution of electronically excited O(^{1}D) atoms produced when ozone photodissociates in the UV Hartley band, centered at 255 nm. Note that O(^{3}P) atoms from the Huggins, Chappuis and Wulf bands will also be very hot translationally [$v(N_2)$ at 200 K ≈ 390 m s^{-1}].

E. Baloïtcha and G. G. Balint-Kurti (2005), Theory of the photodissociation of ozone in the Hartley continuum; effect of vibrational excitation and O(^{1}D) atom velocity distribution, *Phys. Chem. Chem. Phys.*, 7, 3829-3833, doi:10.1039/b511640f.

Microscopic - Macroscopic Interplay

The basic molecular equations are largely intractable to an analytical approach to deriving hydrodynamics, so molecular dynamics simulations have been the way forward (B J Alder and co-workers).

The atmosphere is far from equilibrium, because of the Gibbs free energy difference arising from the entropy difference between the incoming beam of photons from a black body at about 5800 K and the outward photon flux over 4π solid angle from a black body at about 250 K.

The atmosphere has anisotropies arising from the solar beam, gravitation, planetary rotation, radiation to and from warmer air, the surface and the larger scale flow.

The assumption that molecular diffusion is the sole transport process at STP on scales that are centimetric and smaller cannot be justified. Whither local thermodynamic equilibrium?

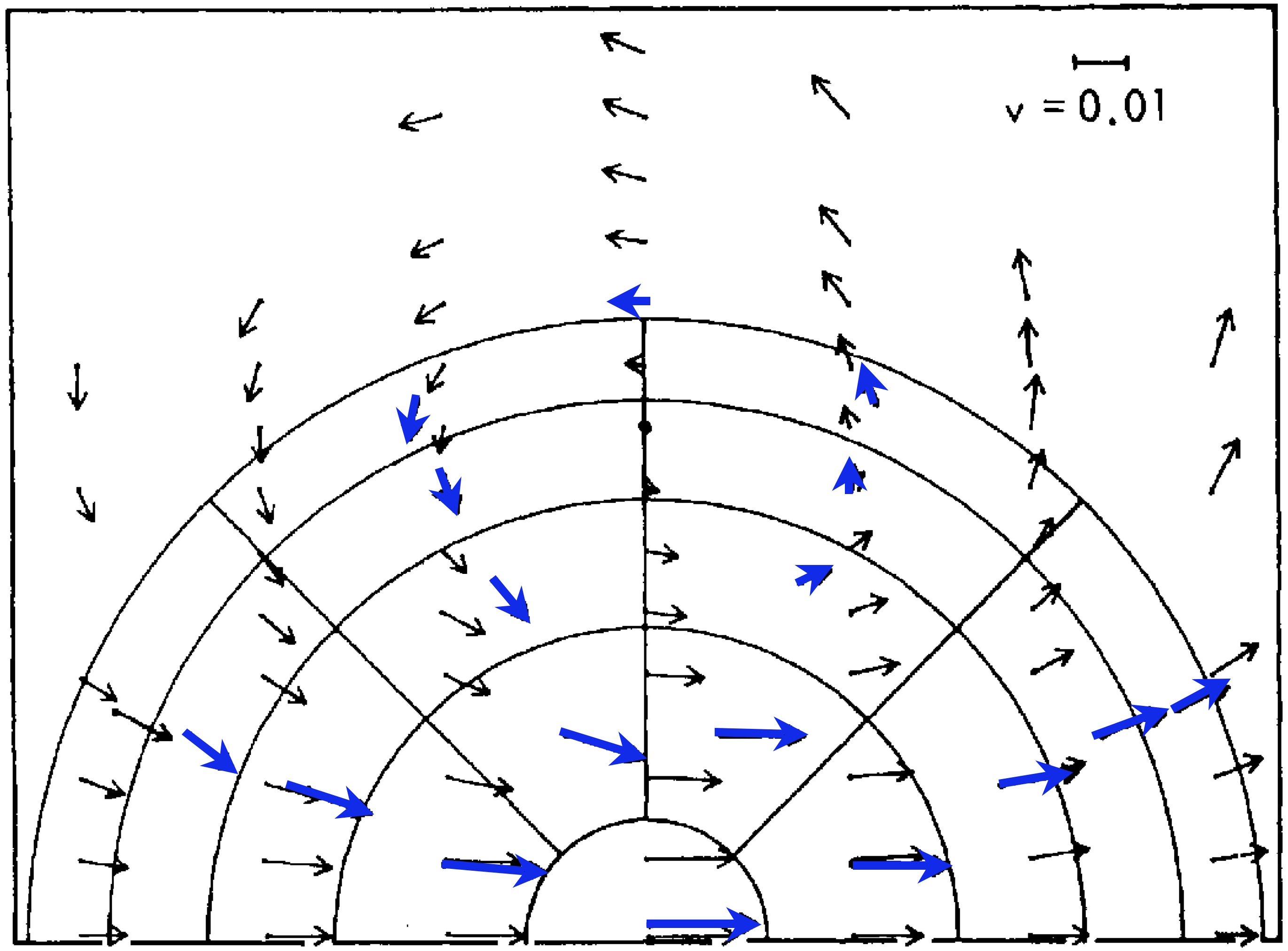
Real atmospheric molecules are not billiard balls!

Observations of temperature can be characterized as a statistical multifractal. The effects of gravity upon temperature are evident in vertical profile data from dropsondes and aircraft (not shown here). Temperature scales differently in the vertical than any other variable.

Alder & Wainwright: MD and Hydrodynamics

Alder & Wainwright's original molecular dynamics (MD) simulation of initially equilibrated Maxwellian atoms with an applied anisotropic flow. Black arrows represent simulation by the Navier-Stokes equation, blue arrows represent averages over the molecular velocity vectors after 9.9 collision times. Some later simulations show disagreement between MD and N-S calculations.

It is very important that 'ring currents' and high-velocity tails of molecular velocities are mutually self-sustaining. Vortices have scale 10 nm and up and are generated on picosecond time scales in response to anisotropy. The fast molecules pile up high number density ahead of them and leave low number density behind them. Translationally hot photofragments from ozone (frame 12) recoil into vorticity structures, not into a 'bath' with a thermalized distribution of molecular velocities.



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Questions & Opportunities

What is atmospheric temperature?

What are the effects of ozone photodissociation on the IR spectra on H_2O and CO_2?

What are the effects on the 'greenhouse' signature of tropospheric warming and stratospheric cooling?

What effects are there on $O(^3P)$ chemistry in particular and chemical kinetics in general?

What are the turbulent implications for transport and mixing?

Opportunities for laboratory experiment.

Opportunities for molecular dynamics simulations.

Opportunities for atmospheric observation.

Small scale observations and laboratory work will be essential.