

Today's Lecture (Lecture 4): Atmosphere – the role of water

Reference

- ▶ Peixoto and Oort, Sec. 3.1, 3.2, 3.4, 3.5

Thermodynamics of the moist atmosphere

Why is the presence of water in the atmosphere important?

- ▶ Phase changes of water
- ▶ Latent heat release → effect on dynamics
- ▶ Cloud formation → effect on radiation
- ▶ Precipitation and evaporation → coupling to land and ocean

Chemical equilibrium

In an open system with multiple species (air, water, ...), the internal energy for the system is $U = U(S, V, n_1, \dots, n_c)$, where n_k is the number of moles of species k , and the combined first and second law is

$$dU = T dS - p dV + \sum_{k=1}^c \mu_k dn_k, \quad \text{where} \quad \mu_k = \left. \frac{\partial U}{\partial n_k} \right|_{S, V, n_{i \neq k}} \quad \text{is called the } \textit{chemical potential}. \quad (2.50)$$

Now consider multiple phases (φ) in equilibrium. The extensive variables U, S, V, n_k are additive, so

$$U = \sum_{\varphi} U^{(\varphi)}, \quad S = \sum_{\varphi} S^{(\varphi)}, \quad V = \sum_{\varphi} V^{(\varphi)}, \quad n_k = \sum_{\varphi} n_k^{(\varphi)} \quad (2.51)$$

Equilibrium is reached when the total internal energy of the system is minimized, i.e., any small change in the independent variables $\delta S^{(\varphi)}, \delta V^{(\varphi)}, \delta n_k^{(\varphi)}$ leads to

$$\delta U = \sum_{\varphi} \left(T^{(\varphi)} \delta S^{(\varphi)} - p^{(\varphi)} \delta V^{(\varphi)} + \sum_k \mu_k^{(\varphi)} \delta n_k^{(\varphi)} \right) \geq 0 \quad \text{subject to} \quad \sum_{\varphi} \delta S^{(\varphi)} = \sum_{\varphi} \delta V^{(\varphi)} = \sum_{\varphi} \delta n_k^{(\varphi)} = 0 \quad (2.52)$$

In the two-phase case (denoted by ' and ''), this requires

$$(T'' - T') \delta S'' - (p'' - p') \delta V'' + \sum_k (\mu_k'' - \mu_k') \delta \mu_k'' \geq 0 \quad (2.53)$$

which can only be satisfied for arbitrary independent $\delta S'', \delta V'', \delta \mu_k''$ if the phases satisfy

$$T'' = T' \text{ (thermal)}, \quad p'' = p' \text{ (mechanical)}, \quad \mu_k'' = \mu_k' \text{ (chemical equilibrium)} \quad (2.54)$$

Phase transition

Consider what happens if we boil water by adding heat to the system; S and V increase while T and p are constant. We can therefore calculate the entropy increase as

$$\Delta S = \frac{\Delta H}{T} \quad \text{or intensively} \quad \Delta s = \frac{\Delta h}{T} = \frac{L}{T} \quad (2.55)$$

L is the *latent heat* of the phase change:

ice \leftrightarrow liquid latent heat of fusion, L_{il}

liquid \leftrightarrow vapor latent heat of vaporization, L_{lv}

ice \leftrightarrow vapor latent heat of sublimation, L_{iv}

Phase equilibria

Now consider two phases in equilibrium (vapor over ice or vapor over liquid) while heat is being added to the system. Invoking the intensive form of the Gibbs–Duhem relation (2.63, derived on the next slide) and making use of the phase equilibrium conditions (2.54) for the two phases (again denoted by ' and '''), we have

$$s' dT - \alpha' dp + d\mu = 0 \quad (2.56)$$

$$s'' dT - \alpha'' dp + d\mu = 0 \quad (2.57)$$

or

$$s' dT - \alpha' dp = s'' dT - \alpha'' dp \quad (2.58)$$

Derivation of the Gibbs–Duhem relation

U, S, V, n_k are extensive, T, p, μ_k are intensive. Therefore, for an arbitrary constant λ ,

$$U(\lambda S, \lambda V, \lambda n_1, \dots, \lambda n_c) = \lambda U(S, V, n_1, \dots, n_c) \quad (2.59)$$

Denoting the extensive variables by x_i and the intensive variables by $y_i = \partial U / \partial x_i$,

$$U(x_1, x_2, \dots) = \frac{d}{d\lambda} U(\lambda x_1, \lambda x_2, \dots) = \sum_i \frac{\partial U(\lambda x_1, \lambda x_2, \dots)}{\partial \lambda x_i} x_i = \sum_i y_i x_i \quad (2.60)$$

so that

$$U(S, V, n_1, \dots, n_c) = TS - pV + \sum_{k=1}^c \mu_k n_k + \text{additive constant} \quad (2.61)$$

Formally,

$$dU = d(TS) - d(pV) + \sum_{k=1}^c d(\mu_k n_k) = T dS + S dT - p dV - V dp + \sum_{k=1}^c \mu_k dn_k + \sum_{k=1}^c n_k d\mu_k \quad (2.62)$$

However, (2.62) is only consistent with the combined first and second law (2.50) if

$$S dT - V dp + \sum_{k=1}^c n_k d\mu_k = 0 \quad (\text{Gibbs–Duhem relation}), \quad (2.63)$$

that is, the state variables cannot all be independent of each other.

Clausius–Clapeyron equation

(2.58) can be transformed to the Clapeyron equation

$$\frac{dp}{dT} = \frac{s'' - s'}{\alpha'' - \alpha'} = \frac{\Delta s}{\Delta \alpha} = \frac{\Delta h}{T \Delta \alpha} = \frac{L}{T \Delta \alpha} \quad (2.64)$$

For the case of water vapor over liquid water or ice, $\alpha_v \gg \alpha_l$ or α_i so that $\Delta \alpha \approx \alpha_v$. The equilibrium pressure p is the saturation water vapor pressure e_s ; if $e > e_s$, water vapor condenses to restore equilibrium, if $e < e_s$ liquid water evaporates to restore equilibrium. Substituting for α_v using the equation of state for water vapor, we find the Clausius–Clapeyron equation

$$\frac{d \ln e_s}{dT} = \frac{L}{R_v T^2} \quad (2.65)$$

Approximating $L \approx \text{const}$, (2.65) can be integrated:

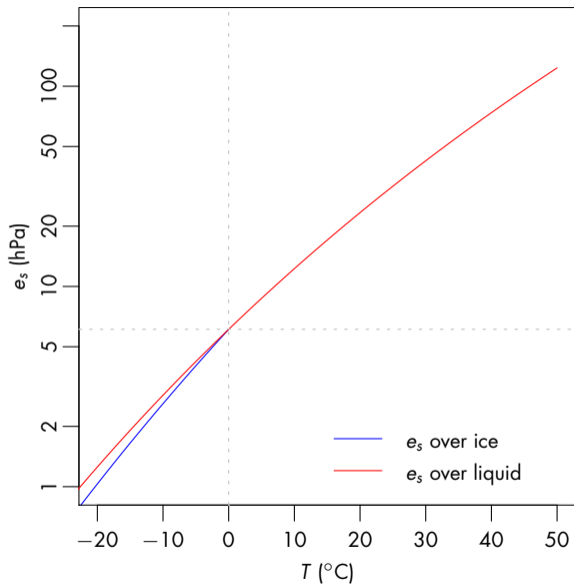
$$e_s = e_{s,0} \exp \left[\frac{L}{R_v} \left(\frac{1}{T_0} - \frac{1}{T} \right) \right] \approx e_{s,0} \exp \left(\frac{L}{R_v} \frac{T - T_0}{T_0^2} \right) \quad (2.66)$$

Consequences of the Clausius–Clapeyron equation

Exponential increase of saturation pressure with temperature ($\times 2$ for every 10 K) combined with

High L of water result in efficient latent heat transport in convection

$L_{iv} > L_{lv}$ results in lower saturation pressure over ice than supercooled water



Convection

Dry adiabatic convection

Consider a parcel of rising air. While the water vapor pressure is below saturation water vapor pressure, adiabatic expansion cools the parcel according to (2.47, with c_{pd} indicating the dry air heat capacity)

$$c_{pd} d \ln T = R_d d \ln p \quad (2.67)$$

which, upon substitution of hydrostatic equilibrium, yields the dry adiabatic lapse rate

$$\Gamma_d = -\frac{\partial T}{\partial z} = \frac{g}{c_{pd}} = \text{const} \quad (2.68)$$

Saturated adiabatic convection

Once the parcel reaches saturation, further expansion results in condensation of water vapor, which releases latent heat:

$$(c_{pd} + q_s c_{pv}) dT + L_{lv} dq_s = (R_d + q_s R_v) \frac{T}{p} dp, \text{ where } q_s \text{ is the mixing ratio (2.16) corresponding to } e_s \quad (2.69)$$

The resulting saturated adiabatic lapse rate, neglecting $q_s c_{pv} \ll c_{pd}$ and $q_s R_v \ll R_d$, is

$$\Gamma_s = -\frac{\partial T}{\partial z} \approx \frac{g}{c_{pd} + L_{lv}(dq_s/dT)} = f(T) \neq \text{const} \quad (2.70)$$

which is always **smaller** than the dry adiabatic lapse rate and **decreases** with increasing temperature. 

Thermodynamic variables for saturated atmospheres

Equivalent potential temperature

From the adiabatic energy balance equation (2.69), this time retaining $q_s c_{pv} \ll c_{pd}$ and $q_s R_v \ll R_d$, we see that the *equivalent potential temperature*

$$\theta_e = \theta_d \exp\left(\frac{L_v q_s}{c_{pd} T}\right) \quad (2.71)$$

is conserved in saturated convection.

Static stability

Depending on the environmental lapse rate Γ , a parcel of air of a certain water vapor mixing ratio will be stable or unstable against vertical perturbation:

$\Gamma > \Gamma_d$ unconditionally unstable: the lifted parcel will always be more buoyant than the ambient air

$\Gamma_d > \Gamma > \Gamma_s$ conditionally unstable depending on lifting condensation level and entrainment

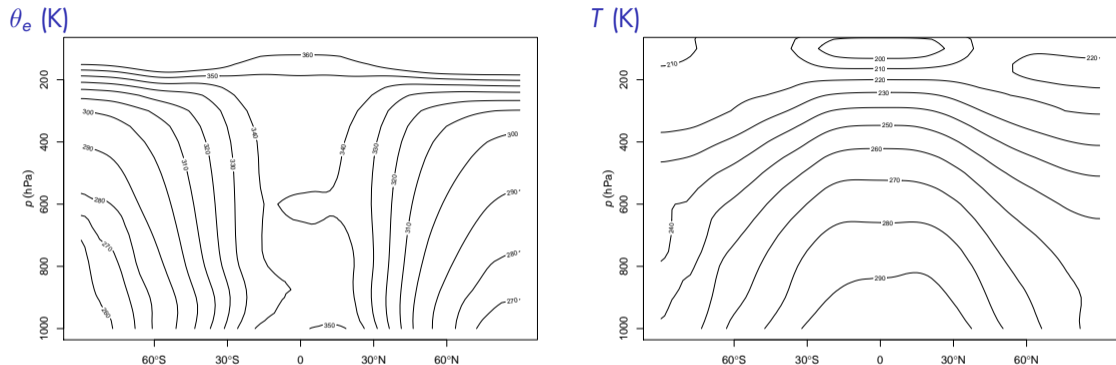
$\Gamma < \Gamma_s$ unconditionally stable: the lifted parcel will always be less buoyant than the ambient air

Static energy

Static energy is the sum of potential and thermal energy, including the latent heat released in the condensation of water vapor ("static" because it does not include the macroscopic kinetic energy):

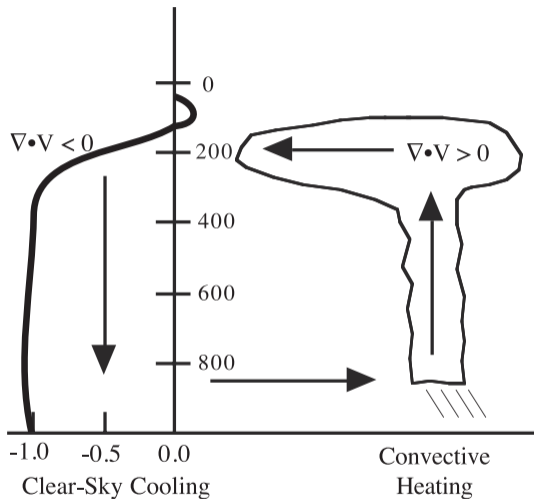
$$h = c_p T + gz + L_v q_l \quad (2.72)$$

The radiative–convective (–advective) equilibrium thermodynamic state of the tropical troposphere



The radiative–convective equilibrium in the tropics results in nearly constant θ_e . Why is this? θ_e is conserved in saturated adiabatic ascent (the rising branch of convection); that is a strong hint that deep clouds play a role. But what about the clear-sky areas?

Balance between vertical motion, radiative cooling and convective heating



Ascending motion (saturated convection)

$$\theta_e = \theta \exp\left(\frac{L_{lv}q_s}{c_{pd}T}\right) = \text{const} \quad (2.73)$$

Subsiding motion (dry convection)

$$c_p \frac{dT}{dt} = T \frac{ds}{dt} + \alpha \frac{dp}{dt} = Q + \alpha \omega,$$

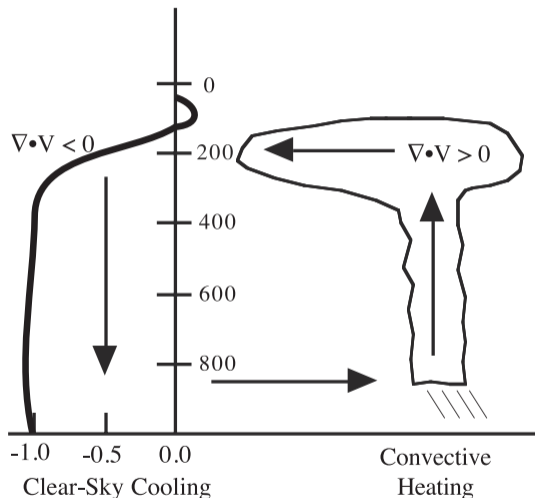
using the definition $\theta = T(p_0/p)^{(R_d/c_p)}$,

$$c_p \frac{T}{\theta} \left(\frac{\partial \theta}{\partial t} + \vec{v} \cdot \nabla \theta + \omega \frac{\partial \theta}{\partial p} \right) = Q \quad (2.74)$$

Steady-state ($\partial/\partial t = 0$), neglecting horizontal advection:

$$c_p \frac{T}{\theta} \omega \frac{\partial \theta}{\partial p} = Q_{\text{rad}} \quad (2.75)$$

Balance between vertical motion, radiative cooling and convective heating



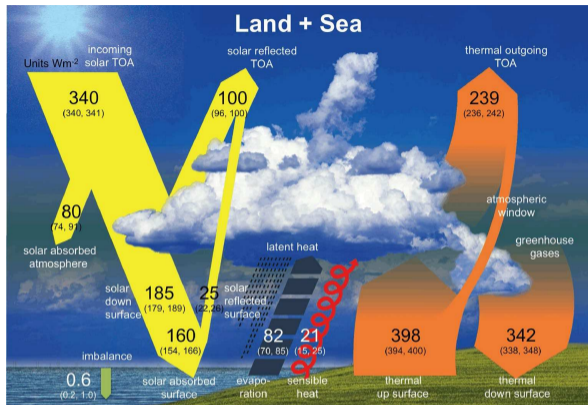
Ascending motion (saturated convection)

- ▶ $Q_{LH} \sim 10 \text{ K day}^{-1}$
- ▶ ω large, area fraction small

Subsiding motion (dry convection)

- ▶ $Q_{\text{rad}} \sim -1 \text{ K day}^{-1}$
- ▶ ω small, area fraction large

Exchange processes of the atmosphere with land and ocean



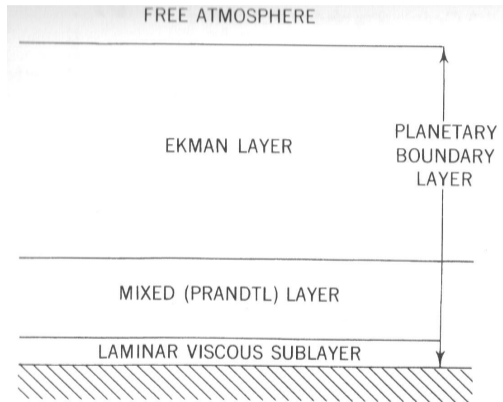
- ▶ Radiative fluxes from surface into atmosphere
- ▶ Momentum dissipation (= momentum source for ocean)
- ▶ Fluxes of sensible heat, latent heat (\propto moisture flux)
- ▶ Orography also influences general circulation

Radiative energy balance of the atmosphere (sign convention: downwelling positive) is

$$R_a = F_{\text{TOA}} - F_s + R_{\text{TOA}} - R_s = (340 - 100) - 160 + (-239) - (342 - 398) \text{ W m}^{-2} = \mathcal{O}(-100 \text{ W m}^{-2}), \quad (2.73)$$

balanced by fluxes of sensible and latent heat into the atmosphere

Boundary layer – the dynamic view



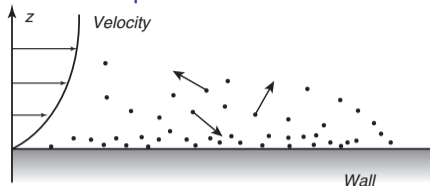
Viscous layer Friction by molecular viscosity: relative motion at the surface is zero, and viscous media resist shearing

Mixed layer Friction by turbulent mixing: momentum transport against the gradient

Ekman layer Both Coriolis force and turbulent friction are important; mean wind speed increases with height, mean wind direction becomes increasingly geostrophic

Free troposphere Geostrophic balance in (mostly) non-turbulent flow

Viscous transport



Viscous friction is due to molecular effects that resist shear in flow. At the surface, the wind velocity must be zero, while in the free stream, the wind velocity will have some arbitrary magnitude. Since random motion of air molecules results in exchange of mass between the low-momentum layers and the high-momentum layers, resulting in the velocity profile shown on the left. The macroscopic friction is the result of the molecular-scale transport of momentum from the free stream into the boundary layer.

The *shear stress* in the fluid in the viscous layer is

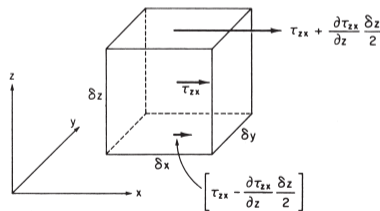
$$\tau_{zx} = -\mu \frac{\partial u}{\partial z} \quad (2.74)$$

(and similarly for τ_{zy} and v), where the subscripts denote the stress is in the x direction in the $z = \text{const}$ plane. The friction in the x direction is

$$F_x = -\frac{1}{\rho} \left(\frac{\partial \tau_{xx}}{\partial x} + \frac{\partial \tau_{yx}}{\partial y} + \frac{\partial \tau_{zx}}{\partial z} \right) \quad (2.75)$$

$$\approx \frac{1}{\rho} \frac{\partial}{\partial z} \left(\mu \frac{\partial u}{\partial z} \right) = \nu \frac{\partial^2 u}{\partial z^2} \quad (2.76)$$

$\nu = \mathcal{O}(10^{-5} \text{ m}^2 \text{ s}^{-1})$, so the depth of the viscous layer is $\ll 1 \text{ m}$.



Turbulent transport

A more efficient method of momentum transport is turbulence. Here the transport is accomplished by small-scale disturbances (u', v', w', θ') in the mean flow $(\bar{u}, \bar{v}, \bar{w}, \bar{\theta})$. The turbulent motions span greater length scales than molecular motion and can support deeper boundary layers. For a vertically sheared layer, the turbulent transport terms take the form $\overline{u'w'}$, $\overline{v'w'}$ for the vertical transport of horizontal momentum, $\overline{\theta'w'}$ for the vertical transport of potential temperature (and thus buoyancy). The transport is against the gradient.

Gradient-flux ansatz

Unlike in the case of viscosity, there is no theoretically well founded way to derive u', v', w', θ' . The best we can do is make a reasonable guess and see how well it works. The English expression for this is "ansatz". In the *gradient-flux ansatz*, the turbulent transport is assumed to be proportional to the gradient:

$$\frac{1}{\rho} \begin{pmatrix} \tau_{zx} \\ \tau_{zy} \end{pmatrix} = \overline{\vec{v}'w'} = -K_m \frac{\partial \vec{v}}{\partial z} \quad \text{and} \quad \overline{\theta'w'} = -K_h \frac{\partial \bar{\theta}}{\partial z} \quad (2.77)$$

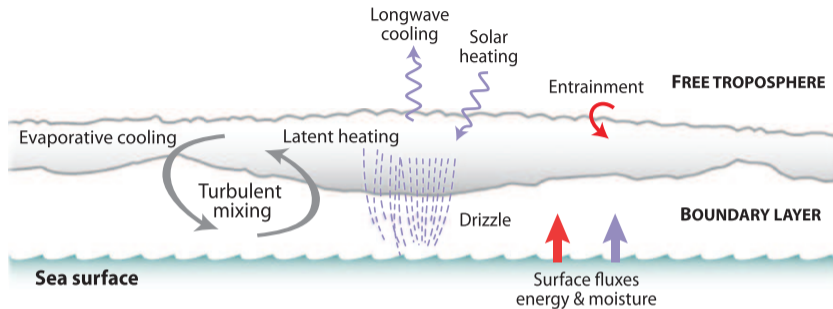
with constant *turbulent diffusion coefficients* for mass and heat K_m and K_h . This formulation is by analogy to viscous friction, but with much larger "viscosity": $K_m = \mathcal{O}(10^{-1} \text{ m}^2 \text{ s}^{-1})$. However, a constant K_m and K_h do not represent the atmospheric boundary layer well because the turbulent length scale grows with distance from the surface.

Mixing-length approach

The next-better refinement is the *mixing-length approach*, where K_m is itself a function of the gradient and a characteristic length scale for mixing. The surface-atmosphere interaction can then be formulated in terms of coefficients of transfer for momentum, sensible heat and water vapor (latent heat)

$$\tau = -\rho C_D |\vec{v}(z)| \vec{v}(z), \quad F_{SH} = -\rho c_p C_H |\vec{v}(z)| \{\theta(z) - \theta(0)\}, \quad E = -\rho C_W |\vec{v}(z)| \{q(z) - q(0)\} \quad (2.78)$$

Boundary layer – the cloud-process view



Vertical structure

Boundary layer is well mixed and capped by a ...

Cloud layer which maintains a temperature inversion by cloud-top cooling and is weakly coupled to the ...

Free troposphere by an entrainment layer

Processes

Sensible and latent heat flux at the surface and ...

Radiative cooling at cloud top destabilize the airmass; this results in ...

Convection which mixes the layer vertically and horizontally

Appendix: Why does dry air have $c_v = \frac{5}{2}RT$?

Recall the partition function (*Zustandssumme*) of the canonical ensemble from statistical mechanics, which is the sum over all microstates weighted by the (Boltzmann) probability of occupying each microstate:

$$Z = \prod_i \int \exp(-\beta H(p_i, q_i)) dp_i dq_i, \quad \beta = \frac{1}{kT} \quad (2.79)$$

where q_i are the canonical positions and p_i the canonical momenta, and H is the hamiltonian of the system. The expectation value of the internal energy U is

$$U = \langle H \rangle = \frac{1}{Z} \prod_i \int H(p_i, q_i) \exp(-\beta H(p_i, q_i)) dp_i dq_i, \quad (2.80)$$

which can be calculated from the partition sum:

$$U = -\frac{1}{\beta} \frac{\partial \ln Z}{\partial \beta}. \quad (2.81)$$

For degrees of freedom that enter the hamiltonian as quadratic terms $H = \sum_i (A_i q_i^2 + B_i p_i^2)$ (for example $H = \frac{1}{2m}(p_x^2 + p_y^2 + p_z^2)$),

$$Z = \prod_i \int_{-\infty}^{\infty} \exp(-\beta A_i q_i^2) dq_i \int_{-\infty}^{\infty} \exp(-\beta B_i p_i^2) dp_i = \prod_i \sqrt{\frac{\pi}{\beta A_i}} \sqrt{\frac{\pi}{\beta B_i}} \quad (2.82)$$

Since

$$-\frac{1}{\beta} \frac{\partial}{\partial \beta} \sqrt{\frac{\pi}{\beta A_i}} = \frac{1}{2} \frac{1}{\beta} = \frac{1}{2} kT \quad \forall A_i, B_i \quad (2.83)$$

the total internal energy is $\frac{1}{2} NkT$ for each degree of freedom that enters quadratically into the hamiltonian. This is the *equipartition theorem*.

How many degrees of freedom does dry air have? At the 99% level, air is a diatomic gas (N_2, O_2). A diatomic molecule has three translational

$$H_{\text{trans}} = \frac{1}{2m} (p_x^2 + p_y^2 + p_z^2)$$

two rotational

$$H_{\text{rot}} = \frac{1}{2} (I_1 \omega_1^2 + I_2 \omega_2^2)$$

and one vibrational

$$H_{\text{vib}} = \frac{1}{2} k \Delta x^2$$

degrees of freedom. Although the energy levels are quantized, the translational and rotational energy levels are closely enough spaced that the classical continuum limit is valid. The vibrational energy levels are much higher than atmospheric temperatures [$\mathcal{O}(10^3)$ K]; the vibrational degree of freedom contributes negligibly to the internal energy.

Therefore,

$$U = \frac{5}{2} NkT \quad \text{and} \quad c_v = \left(\frac{\partial u}{\partial T} \right)_v = \frac{5}{2} R_d \quad (2.84)$$