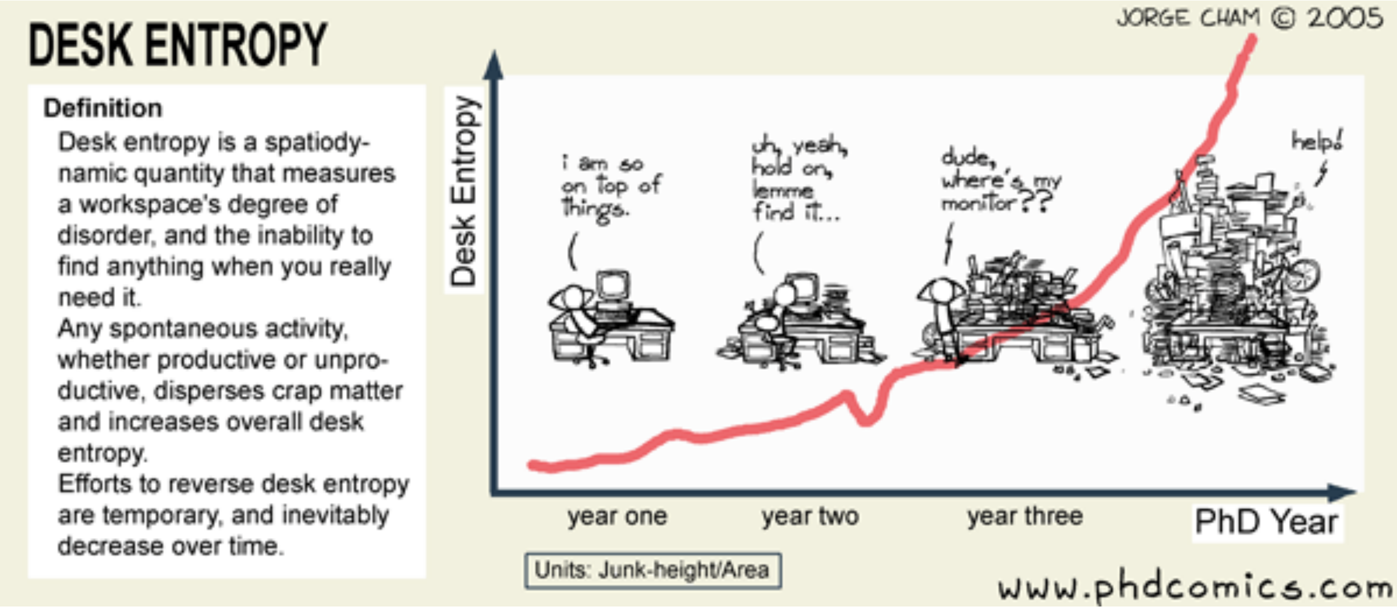
Thermodynamics Review [?]

- Entropy & thermodynamic potentials
- Hydrostatic equilibrium & buoyancy
- Stability [dry & moist adiabatic]

Entropy

- 1. (Thermodynamics) a thermodynamic quantity that changes in a reversible process by an amount equal to the heat absorbed or emitted divided by the thermodynamic temperature. It is measured in joules per kelvin [J/K].
- 2. (Statistical Physics) a statistical measure of the disorder of a closed system expressed by $S = k_B \log W + c$ where W is the probability that a particular state of the system exists, and c is an arbitrary constant
- 3. (General Physics) lack of pattern or organization; disorder
- 4. (Electronics & Computer Science / Communications & Information) a measure of the efficiency of a system, such as a code or language, in transmitting information



Definition

Desk entropy is a spatiodynamic quantity that measures a workspace's degree of disorder, and the inability to find anything when you really need it.

Any spontaneous activity, whether productive or unproductive, disperses crap matter and increases overall desk entropy.

Efforts to reverse desk entropy are temporary, and inevitably decrease over time.

1st Law of Thermodynamics & Thermodynamic Identity

$$du = d'q - d'w$$

The notation d′ denotes an inexact differential, i.e., an integral over the quantity depends on the path taken.

(1) 1st Law ⇔ Energy conservation: the change in energy of a system *du* must equal the heat added to/removed from the system *d′q* and the work done on/by the system *d′w*.

$$s(u,\{x_i\}) \Longrightarrow \left(\frac{\partial s}{\partial u}\right)_{\{x_i\}} = \frac{1}{T}$$

(2) Definition of temperature [from entropy *s*, which is written as a function of *u* and a set of other variables *{x$_i$}*]

$$ds = \left(\frac{\partial s}{\partial u}\right)_{\{x_i\}} du + \left(\frac{\partial s}{\partial x_i}\right)_{u,\{x_{n\neq i}\}} dx_i$$

Expanding *s* as a linear function of it’s first partial derivatives…

$$du = Tds - T\left(\frac{\partial s}{\partial x_i}\right)_{u,\{x_{n\neq i}\}} dx_i$$

… and rearranging, using (2)…

$$du = Tds + T\left(\frac{\partial s}{\partial \alpha}\right)_u d\alpha = Tds - pd\alpha$$

$$= d'q - d'w$$

… leads to (3) the thermodynamic identity.

Here, pressure p is related to the partial derivative of s w.r.t. system volume.

Aside: Thermodynamic Potentials

Potential: generalized "force" F_i multiplied by a generalized "displacement" d_i:

$$\Phi = F_i d_i$$

Internal energy (*U*):

$$U = U(S,V,\{N_i\}) = TS - pV + \boxed{\mu_i N_i}$$

Helmholtz free energy (*A*):

$$A = A(T,V,\{N_i\}) = U - TS$$

Chemical potential (μ_i): force related to particle exchange (of species i) between systems

Gibbs free energy (*G*):

$$G = G(T,p,\{N_i\}) = U - TS + pV$$

Enthalpy (*H*):

$$H = H(S,p,\{N_i\}) = U + pV$$

Landau or Grand Potential (*Ω*):

$$\Omega = \Omega(T,V,\{\mu_i\}) = U - TS - \mu_i N_i$$

- *Euler's homogeneous function theorem* allows *U* to be written in terms of *TS*, *pV*, …
- T,p,μ_i are *intensive* variables: they are unchanged if 2 or more identical systems are combined. S,V,N_i [and, e.g., *U*] are extensive, scaling with system size.
- *Legendre transforms* applied to obtain other potentials
- Properties of potentials can be exploited for different purposes, e.g., Gibbs is useful for processes in *T*-*p* space.
- *Maxwell relations*: equivalence of mixed partial derivatives

Hydrostatic equilibrium & buoyancy

Newton's 2nd Law of Motion in the z direction:

$$\vec{F} = m\vec{a}$$

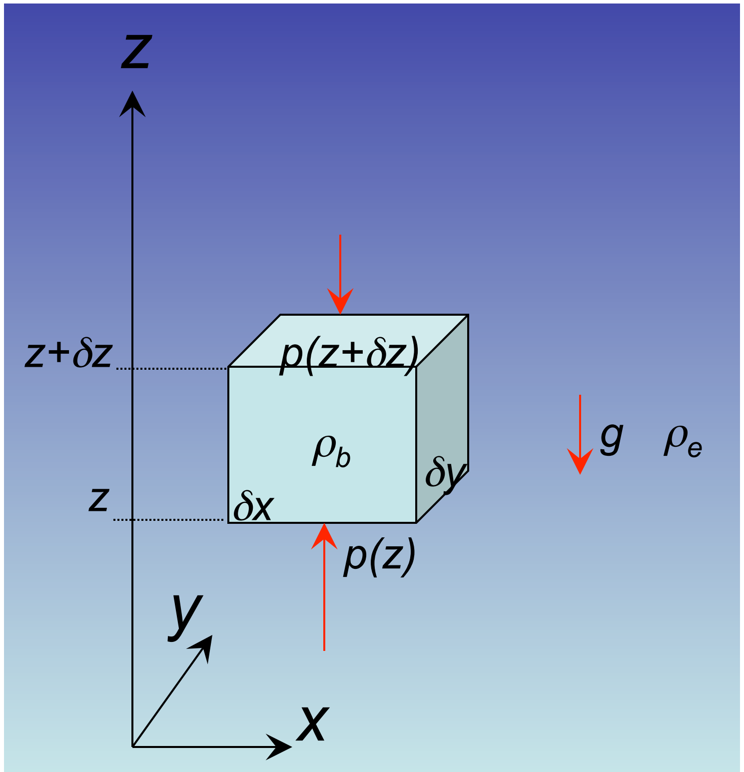
Consider first the case with equal environmental and parcel densities, i.e., $\rho_e = \rho_b = \rho$

$$(\rho\delta x\delta y\delta z)\frac{d^2\delta z}{dt^2} =$$

$$-(\rho\delta x\delta y\delta z)g + p(z)\delta x\delta y - p(z+\delta z)\delta x\delta y$$

In equilibrium, and applying limit δz→0,

$$0 = -\rho g - \frac{\partial p}{\partial z}$$



Consider now $\rho_e \neq \rho_b$:

$$(\rho_b\delta x\delta y\delta z)\frac{d^2\delta z}{dt^2} = -(\rho_b\delta x\delta y\delta z)g + p(z)\delta x\delta y - p(z+\delta z)\delta x\delta y$$

$$\Rightarrow \frac{d^2\delta z}{dt^2} = -g + \frac{1}{\rho_b}\frac{\partial p}{\partial z} = -g\left(1 - \frac{\rho_e}{\rho_b}\right) \equiv B$$ Buoyancy

Relating buoyancy and entropy

Defining the specific volume α as $\alpha = \frac{1}{\rho}$, we can rewrite the buoyancy as:

$$B = -g\left(1 - \frac{\rho_e}{\rho_b}\right) = -g\left(1 - \frac{\alpha_b}{\alpha_e}\right) = g\left(\frac{\alpha_b - \alpha_e}{\alpha_e}\right) = g\frac{\Delta\alpha}{\alpha}$$

where $\alpha \equiv \alpha_e$ and $\Delta\alpha \equiv \alpha_b - \alpha_e$

Consider $\alpha=\alpha(s,p)$. Then, at constant pressure:

$$d\alpha = \left.\frac{\partial\alpha}{\partial s}\right|_p ds = \left.\frac{\partial T}{\partial p}\right|_s ds$$

α is equivalent to specific enthalpy, h. The second equality here thus follows from the "Maxwell relations" for mixed second partial derivatives of h.

Thus,

$$B = g\frac{\Delta\alpha}{\alpha} = \frac{g}{\alpha}\left.\left(\frac{\partial T}{\partial p}\right)\right|_s ds = -\left.\frac{\partial T}{\partial z}\right|_s ds = \Gamma ds$$

Use the hydrostatic relationship to covert derivative to a function of z.

Dry adiabatic lapse rate

Adiabatic parcel + ideal gas law [+hydrostatic eq]…

$$Tds = 0 = du + pd\alpha$$

For an ideal gas, the internal energy is a function of T only.

$$p\alpha = R_d T \qquad [R_d \equiv 287\,Jkg^{-1}K^{-1}]$$

…leads to the dry adiabatic lapse rate γ_d:

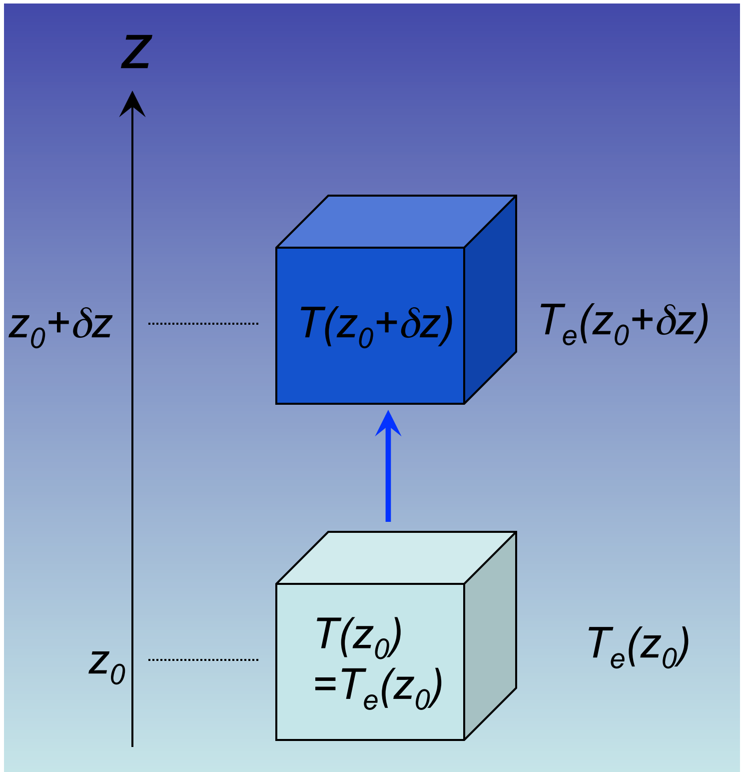
$$\gamma_d = -\left(\frac{\partial T}{\partial z}\right)_{dS=0} = \frac{g}{c_p} \approx 10K/km \qquad [c_p \equiv 1004\,Jkg^{-1}K^{-1}]$$

From the 1D force equation in the vertical [again applying the ideal gas law]:

$$\frac{dw}{dt} = g\frac{\rho_e - \rho}{\rho} = g\frac{T - T_e}{T_e}$$

$$\Big\Downarrow \qquad \Longleftarrow \qquad \begin{aligned} T(z_0+\delta z) &\approx T_e(z_0) - \gamma_d \delta z \\ T_e(z_0+\delta z) &\approx T_e(z_0) - \gamma_e \delta z \end{aligned}$$

$$\frac{dw}{dt} = g\delta z(\gamma_e - \gamma_d)/T_e$$



(Dry) Static Stability

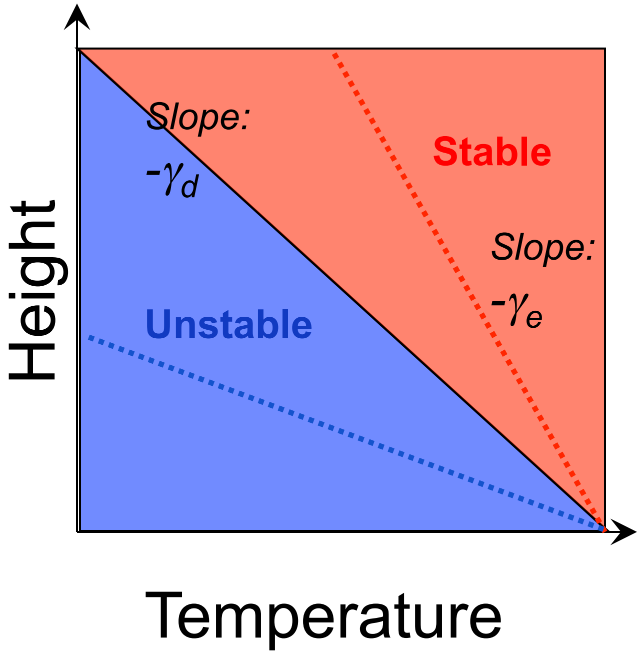
$$w = \frac{d\delta z}{dt} \Rightarrow \frac{d^2\delta z}{dt^2} - \left(g\frac{\gamma_e - \gamma_d}{T_e} \right)\delta z = 0$$

$$\frac{d^2\delta z}{dt^2} + N^2(z)\delta z = 0 \qquad N(z) = \sqrt{-g\frac{\gamma_e - \gamma_d}{T_e(z)}}$$

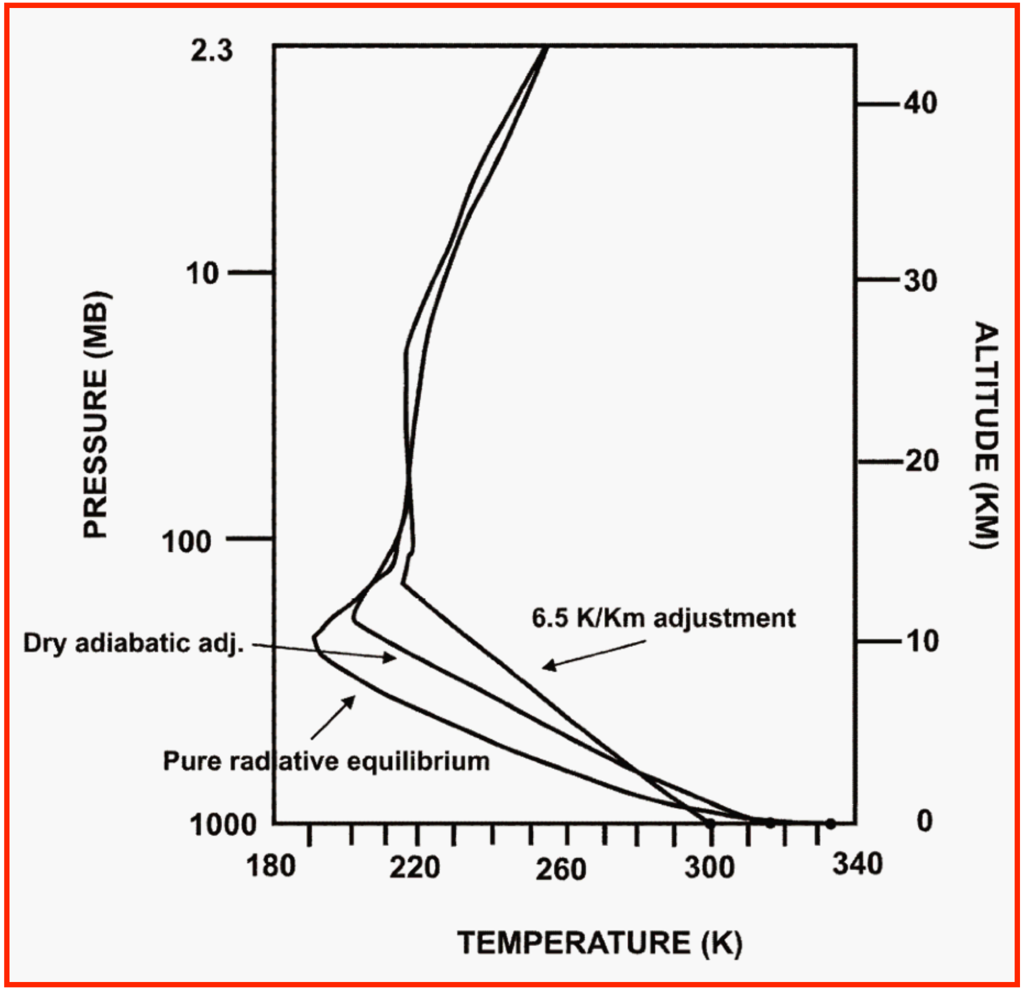
N is known as the *Brunt-V äisälä* frequency.

If $\gamma_e < \gamma_d$, $N^2(z) > 0$, so solutions to the perturbation equation are oscillatory (sinusoids). In this case, the equilibrium is *stable*.

If $\gamma_e > \gamma_d$, $N^2(z) < 0$, so solutions to the perturbation equation are exponential (hyperbolic sine/cosine). In this case, the equilibrium is *unstable*.



Let’s re-evaluate radiative equilibrium



Emanuel, 2005

- Pure radiative equilibrium is in fact unstable for conditions in the troposphere [but is reasonable in the stratosphere].
- Tropospheric γ_d significantly exceeds the observed lapse rate (~6.5K/km)
  - Need to account for vertical heat transport via convection [more shortly and later]

Moist atmosphere

Ideal gas law for dry air (denoted $_d$) and water vapor (denoted $_v$):

$$p_d \alpha_d = R_d T$$
$$e \alpha_v = R_v T$$

$$\left[\frac{R_d}{R_v} = \frac{m_v}{m_d} \approx \frac{18}{28.9} = 0.622\right]$$

The total pressure of moist (dry +vapor) air [Dalton's Law of Partial Pressures]:

$$p = p_d + e$$

The density of moist air is:

$$\rho = \rho_d + \rho_v = \frac{p}{R_d T}\left(1 - 0.378\frac{e}{p}\right)$$

Virtual temperature (T_v): temperature to which dry air must be raised to have the same density as moist air @ the same pressure

$$T_v = T\left[1 - 0.378\frac{e}{p}\right]^{-1}$$

Specific humidity (q):

$$q = \frac{\rho_v}{\rho} = \frac{0.622e}{p - 0.378e} \approx 0.622\frac{e}{p}$$

Using the definitions of q and T_v, the equation of state of moist air is approximately:

$$p \approx \rho R_d T(1 + 0.61q)$$

Saturation

Consider the relative humidity (rh): $rh = \frac{e}{e_s}$

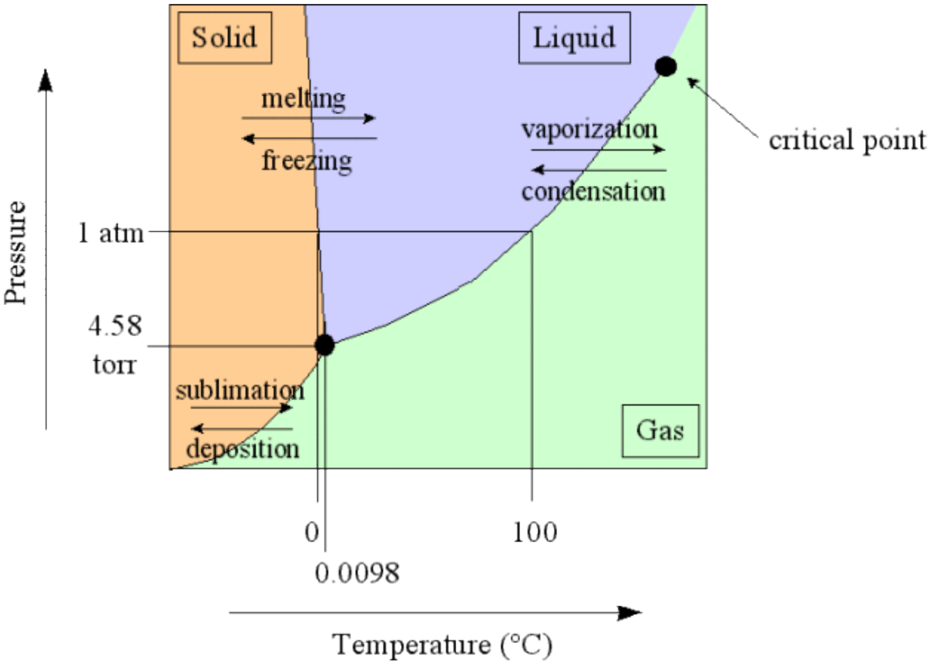
Here, the saturation vapor pressure (e_s) is the maximum vapor pressure attainable at a given temperature

The *Clausius-Clapeyron* equation governs the temperature dependence of e_s for two-phase equilibrium:

$$\frac{de_s}{T} = \frac{L}{T(\alpha_2 - \alpha_2)}$$

If 1 denotes the condensed phase (solid or liquid) and 2 the gaseous phase, $\alpha_2 >> \alpha_1$. From prior definitions and after integration:

$$e_s(T) \propto \exp\left[-0.622 \frac{L}{R_d T}\right]$$



Adiabatic process in a moist atmosphere

Consider first the potential temperature for dry air, θ, which is the temperature a parcel of air would have if displaced, adiabatically and reversibly, to a reference pressure p_0 [typically, 1000 mb]:

$$\theta = T\left(\frac{p_0}{p}\right)^{\kappa}\ ;\kappa = \frac{R_d}{c_p}$$

[To derive: apply 1st law for an adiabatic process ($ds=0$), use definition of internal energy and ideal gas law, and integrate.]

The (dry) entropy can be expressed in terms of θ:

$$\Delta s_d = c_p \ln\theta \qquad d\Delta s_d = 0 \Leftrightarrow d\theta = 0$$

Note: the Δ notation indicates entropy is defined up to an arbitrary constant, i.e., $\Delta s_d = s_d$-constant.

Now, for an adiabatic upward displacement of *saturated* air, condensation will occur, leading to a release of latent heat in the amount $-Ldq_s$. The entropy change associated with this release is $d\Delta s_c = (-Ldq_s)/T$. Equating $d\Delta s_d$ and $d\Delta s_c$ and integrating gives the equivalent potential temperature θ_e:

$$c_p d\ln\theta = -\frac{L_c dq_s}{T} \approx -d\left(\frac{L_c q_s}{T}\right) \qquad \theta_e = \theta\exp\left[\frac{Lq_s}{c_p T}\right]$$

Moist Stability

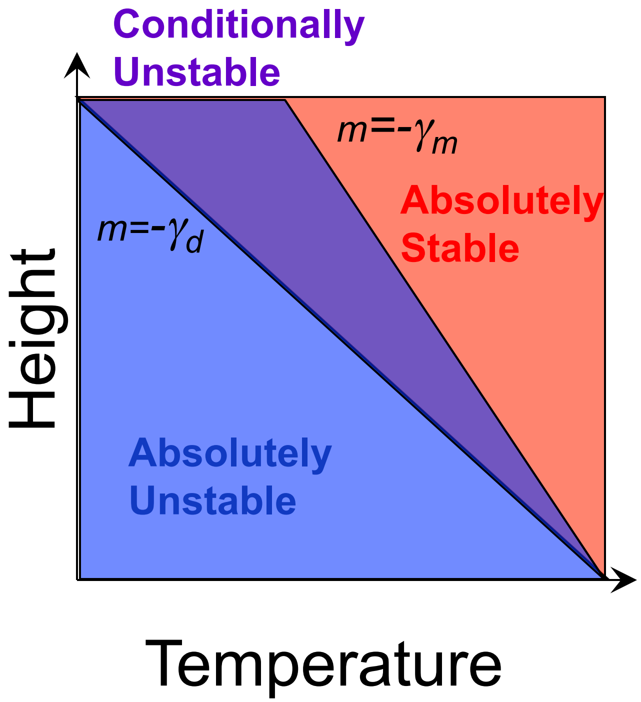
Starting with the vertical acceleration and using the definition of potential temperature, it can be shown that:

$$\frac{d^2\delta z}{dt^2} + N^2(z)\delta z = 0 \Rightarrow \frac{d^2\delta z}{dt^2} + \left(\frac{g}{\theta}\frac{\partial\theta}{\partial z}\right)\delta z = 0$$

Thus: $\frac{\partial\theta}{\partial z} > 0$ *Stable*

$\frac{\partial\theta}{\partial z} < 0$ *Unstable*

Equivalent potential temperature can be used to evaluate stability for a moist atmosphere; by analogy, a moist adiabatic lapse γ_m rate can be defined. A region of conditional instability emerges, for $\gamma_m < \gamma_e < \gamma_d$. For unsaturated air, this region is stable; for saturated air, it's unstable.



Overview of convection [more later]

- Convection is an important source of atmospheric heating associated with H_2O phase changes.
- Vertical motion field associated with convection is an important control on the space-time behavior of H_2O vapor, other tracers, aerosols, and clouds.
- *Global* hydrologic cycle balance implies balance between *global* mean precipitation and evaporation rates [~3 mm day^{-1}]…although significant regional [sub-global] heterogeneity exists.
- Evaporation [aka latent heating] is an important component of the surface energy budget.

Convective adjustment

- Eliminates atmospheric column instability
- Environmental conditions that favor instability:
  - **Cooling** aloft via cold air advection or longwave radiative cooling
  - **Warming** of surface via warm air advection or solar heating
  - *Lifting* of air mass through low-level convergence