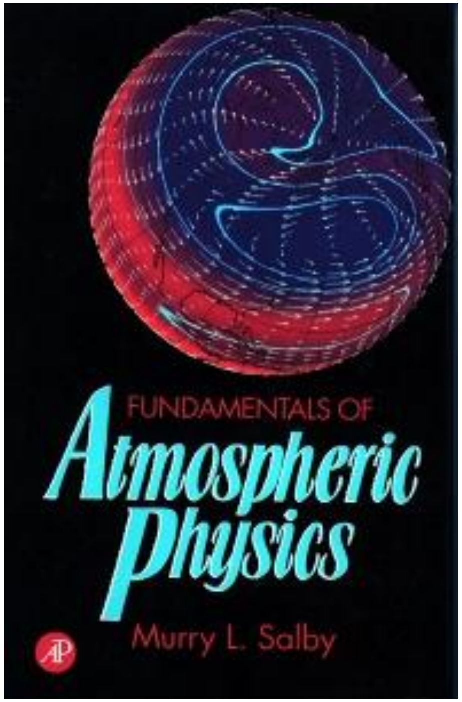
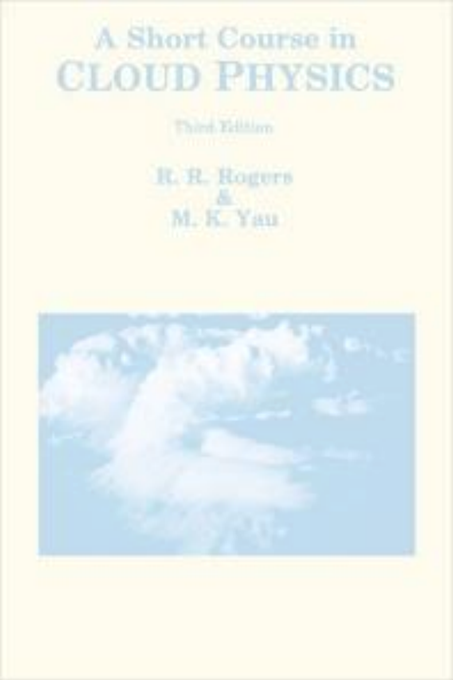
LECTURE OUTLINE

1. The second law of thermodynamics
2. The fundamental relations
3. Conditions for thermodynamic equilibrium

Salby, Chapter 2 and 3

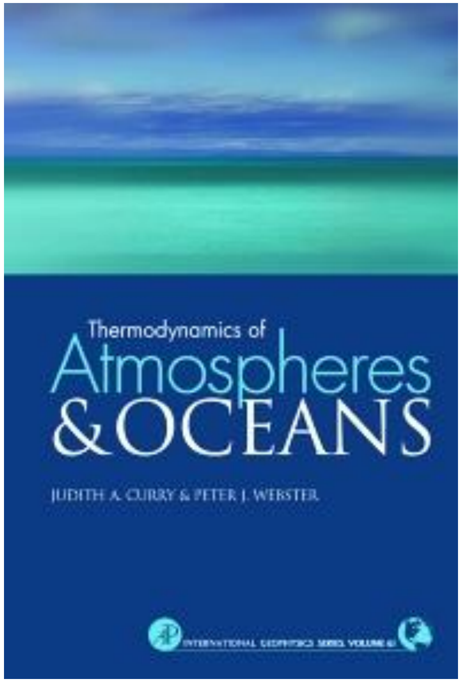


Fundamentals of Atmospheric Physics,
M.L. Salby; Salby


A Short Course in
CLOUD PHYSICS
Third Edition
R. R. Rogers
&
M. K. Yau

A Short Course in Cloud Physics,
R.R. Rogers and M.K. Yau; R&Y

C&W, Chapter 2



Thermodynamics of Atmospheres
and Oceanes,
J.A. Curry and P.J. Webster; C&W

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1. The second law of thermodynamics
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Second Law of Thermodynamics

The second law of thermodynamics forbids certain processes, even some in which energy is conserved.

The second law of thermodynamics may be stated in several different ways.

The entropy statement of the second law is:

There exist an additive function of state known as the **equilibrium entropy**, which can never decrease in a thermally isolated system.

$$ds \geq \left(\frac{\delta q}{T}\right)$$

the equality holds if the process is reversible.

For an adiabatic process the equation reduces to: $ds \geq 0$, so the entropy can only increase.

Letting the control surface of a hypotetical system pass to infinity eliminates heat transfer to the environment and leads to the conclusion that the entropy of the universe can only increase.

$ds \geq \frac{\delta q}{T}$ defines the upper limit of heat that can be absorbed by a system in reversible process: $\delta q \leq Tds, \quad Tds = \delta q_{rev}$.

$ds \geq \frac{\delta q}{T}$ indicates the direction of thermodynamic processes.

Through the inequality, the second law asserts whether or not a system is capable of evolving along a given path.

A process for which the change of entropy satisfies the inequality $\delta q \leq Tds$ is possible.

If the relation is satisfied through equality, that process is reversible, whereas if it is satisfied through inequality that process is irreversible (e.g. a natural process).

A process that satisfies the reverse inequality is impossible: $\delta q > Tds$.

Substituting the second law into the two forms of the first law: $ds \geq \frac{\delta q}{T} \quad \Rightarrow \quad \delta q \leq Tds$

$$du = \delta q - pdv$$
$$dh = \delta q + vdp$$

For irreversible processes:

$$du < Tds - pdv$$
$$dh < Tds + vdp$$

For reversible processes :

$$du = Tds - pdv$$
$$dh = Tds + vdp$$

The above equalities involve only state variables, therefore they cannot depend on path.

They must hold whether or not the process is reversible.

They are known as fundamental relations.

Even though generally valid, the fundamental relations cannot be evaluated easily under irreversible conditions.

$$du = Tds - pdv$$
$$dh = Tds + vdp$$

The values of p and T refer to the pressure and temperature „of the system”, which can be specified only under reversible conditions.

Under irreversible conditions, the relationship among these variables reverts to inequalities, wherein p and T denote „applied values”, which can be specified.

$$du < Tds - pdv$$
$$dh < Tds + vdp$$

Noncompensated heat transfer

The inequalities in fundamental realtions account for additional heat rejections to the environment that occurs through irreversibility.

Those inequalities can be eliminated in favor of equalities by introducing the noncompensated heat transfer $\delta q' > 0$:

$$\delta q = \delta q_{rev} - \delta q' \qquad \delta q_{rev} = Tds$$

$$\delta q = Tds - \delta q'$$

$$du = (Tds - \delta q') - pdv$$

For reversible process: $$du = T_{rev}ds - p_{rev}dv$$

Substratcting gives: $$\delta q' = (T - T_{rev})ds - (p - p_{rev})dv$$

T_{rev} and p_{rev} refer to applied values under equilibrium conditions (i.e. assumed by the system when the process is executed reversibly).

Noncompensated heat transfer results from the thermal disequilibrium of the system, which is represented in the difference $T - T_{rev}$ and from the mechanical disequilibrium of the system, which is represented in the difference $p - p_{rev}$.

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It is convenient to introduce two new state variables:

- The Helmholtz function: $f = u - Ts$ $\quad du = Tds - pdv$

  $$df = -sdT - pdv$$

- The Gibbs function: $g = h - Ts$ $\quad dh = Tds + vdp$

  $$dg = -sdT + vdp$$

Internal energy: $du = Tds - pdv$

Enthalpy: $dh = Tds + vdp$

Helmholtz function (Helmholtz energy): $df = -sdT - pdv$

Gibbs function (Gibbs energy): $dg = -sdT + vdp$

The Helmholtz and Gibbs function are each referred to as the free energy of the system.

The Maxwell relations

Variables appearing in fundamental relations are not entirely independent.

Involving only state variables, each fundamental relation has the form of an exact differential: $M(x,y)dx + N(x,y)dy = dz$

The cross derivatives of the coefficients on the right-hand sides must be equal: $\frac{\partial M}{\partial y} = \frac{\partial N}{\partial x}$

These relations are known as the Maxwell relations

$$\left(\frac{\partial T}{\partial v}\right)_s = -\left(\frac{\partial p}{\partial s}\right)_v \qquad du = Tds - pdv$$

$$\left(\frac{\partial T}{\partial p}\right)_s = \left(\frac{\partial v}{\partial s}\right)_p \qquad dh = Tds + vdp$$

$$\left(\frac{\partial s}{\partial v}\right)_T = \left(\frac{\partial p}{\partial T}\right)_v \qquad df = -sdT - pdv$$

$$\left(\frac{\partial s}{\partial p}\right)_T = -\left(\frac{\partial v}{\partial T}\right)_p \qquad dg = -sdT + vdp$$

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By defining the direction of thermodynamic processes, the second law implies whether or not a path out of a given thermodynamic state is possible; it characterizes the stability of thermodynamic equilibrium.

Consider a system in a given thermodynamic state. An arbitrary infinitesimal process emanating from that state is referred to as a virtual process.

The system is said to be in stable or true equilibrium if no virtual process emanating from that state is a natural process, i.e., if all virtual paths out of that state are either reversible or impossible.

If all virtual paths out of the state are natural processes, the system is said to be in unstable equilibrium. A small perturbation will then result in a finite change of state.

If some of the virtual processes out of the state are natural, the system is said to be in metastable equilibrium. A small perturbation then may or may not result in a finite change of state, depending on the details of the perturbation.

$$ds \geq \left(\frac{\delta q}{T}\right) \longrightarrow \delta q \leq Tds$$

$$du = \delta q - pdv \longrightarrow du \leq Tds - pdv$$

Equality for reversible processes.

Inequality for irreversible (natural) processes.

$$du \leq Tds - pdv$$
$$dh \leq Tds + vdp$$
$$df \leq -sdT - pdv$$
$$dg \leq -sdT + vdp$$

Thermodynamic equilibrium.

Inequailty describes impossible processes.

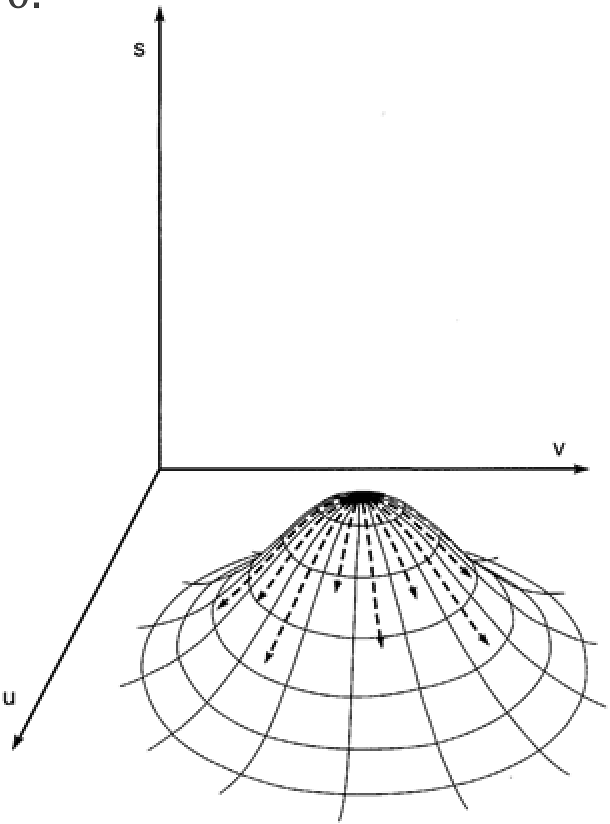
$$du \geq Tds - pdv$$
$$dh \geq Tds + vdp$$
$$df \geq -sdT - pdv$$
$$dg \geq -sdT + vdp$$

Thermodynamic equilibrium in adiabatic processes

For an adiabatic enclosure the second law of thermodynamics $ds \geq \frac{\delta q}{T}$ reduces to $ds \geq 0$ where inequality corresponds to a natural process.

The criterion of thermodynamic equilibrium is: $ds_{ad} \leq 0$.

and describes reversible and impossible processes. .



A state of thermodynamic equilibrium for an adiabatic system coincides with a local maximum of entropy.

An adiabatic system's entropy must increase as it approaches thermodynamic equilibrium.

In thermodynamic equilibrium all virtual paths out of the state are either reversible or impossible.

$$du \geq Tds - pdv$$
$$dh \geq Tds + vdp$$
$$df \geq -sdT - pdv$$
$$dg \geq -sdT + vdp$$

Choosing processes for which the right-hand sides of equations vanish yields another criteria for thermodynamic equilibrium.

$$du_{s,v} \geq 0 \qquad dh_{s,p} \geq 0 \qquad df_{T,v} \geq 0 \qquad g_{T,p} \geq 0$$

The state of thermodynamic equilibrium coincides with local minima in the properties u, h, f, and g.

$$du_{s,v} = 0 \quad d^2u_{s,v} > 0 \qquad dh_{s,p} = 0 \quad d^2h_{s,p} > 0$$

$$df_{T,v} = 0 \quad d^2f_{T,v} > 0 \qquad dg_{T,p} = 0 \quad d^2g_{T,p} > 0$$

Entropy

Entropy is a state variable; it can be expressed by any two intensive parameters, i.e. T and p:

$$ds = \left(\frac{\partial s}{\partial T}\right)_p dT + \left(\frac{\partial s}{\partial p}\right)_T dp$$

A change of entropy from the first law:

$$dh = Tds + vdp \quad \longrightarrow \quad ds = \frac{1}{T}dh - \frac{v}{T}dp \quad \longrightarrow \quad ds = \frac{1}{T}\left(\frac{\partial h}{\partial T}\right)_p dT + \frac{1}{T}\left[\left(\frac{\partial h}{\partial p}\right)_T - v\right] dp$$

$$\uparrow$$

Entalpy is also a state variable; it can be expressed by any two intensive parameters:

$$dh = \left(\frac{\partial h}{\partial T}\right)_p dT + \left(\frac{\partial h}{\partial p}\right)_T dp$$

For $p = const$ the terms multiplying dT must be equal:

$$\left(\frac{\partial s}{\partial T}\right)_p = \frac{1}{T}\left(\frac{\partial h}{\partial T}\right)_p = \frac{c_p}{T}$$

From a Maxwell relation:

$$(dg = -sdT + vdp)$$

$$\left(\frac{\partial s}{\partial p}\right)_T = \left(\frac{\partial v}{\partial T}\right)_p$$

$$\uparrow$$

$$\left(\frac{\partial s}{\partial p}\right)_T = v\alpha_p$$

$$\alpha_p = \frac{1}{v}\left(\frac{\partial v}{\partial T}\right)_p$$

isobaric coefficient of thermal expansion

Entropy

$$ds = c_p d\ln T - v\alpha_p dp \qquad \alpha_p = \frac{1}{v}\left(\frac{\partial v}{\partial T}\right)_p$$ isobaric coefficient of thermal expansion

All parameters on the right-hand side are measurable

The change of entropy can be presented as a function of temperature, T, and specific volume,v.

The derivation of that relation is simillar as presented before, but with the use of the first law in form of internal energy.

$$ds = c_v d\ln T + p\alpha_v dv \qquad \alpha_v = \frac{1}{p}\left(\frac{\partial p}{\partial T}\right)_v$$ isochoric coefficient of thermal expansion

Entropy

For the ideal gas the formulation of entropy takes simpler forms:

$$pv = RT$$

$$\alpha_p = \frac{1}{v}\left(\frac{\partial v}{\partial T}\right)_p = \frac{1}{v}\frac{R}{p} = \frac{1}{T}$$

$$\alpha_v = \frac{1}{p}\left(\frac{\partial p}{\partial T}\right)_v = \frac{1}{p}\frac{R}{v} = \frac{1}{T}$$

$$ds = c_p \mathrm{dln}T - v\alpha_p dp$$

$$ds = c_p \mathrm{dln}T - R\mathrm{dln}p$$

$$ds = c_v \mathrm{dln}T + p\alpha_v dv$$

$$ds = c_v \mathrm{dln}T + R\mathrm{dln}v$$

$$\theta = T\left(\frac{p_0}{p}\right)^{R/c_p} \longrightarrow \mathrm{dln}\theta = \mathrm{dln}T - \frac{R}{c_p}\mathrm{dln}p$$

$$ds = c_p \mathrm{dln}\theta$$

Implication of Second Law for vertical motion

If a process is adiabatic, dθ=0, and ds≥0. The entropy remains constant or it can increase through irreversible work (e.g., that associated with frictional dissipation of kinetic energy).

In the case of air parcel, the conditions for adiabatic behaviour are closely related to those for reversibility.

Adiabatic behaviour requires not only no heat to be transferred across the control surface, but also that no heat is exchanged between one part of the system and another.

The latter excludes turbulent mixing, which is the principal form of mechanical irreversibility in the atmosphere.

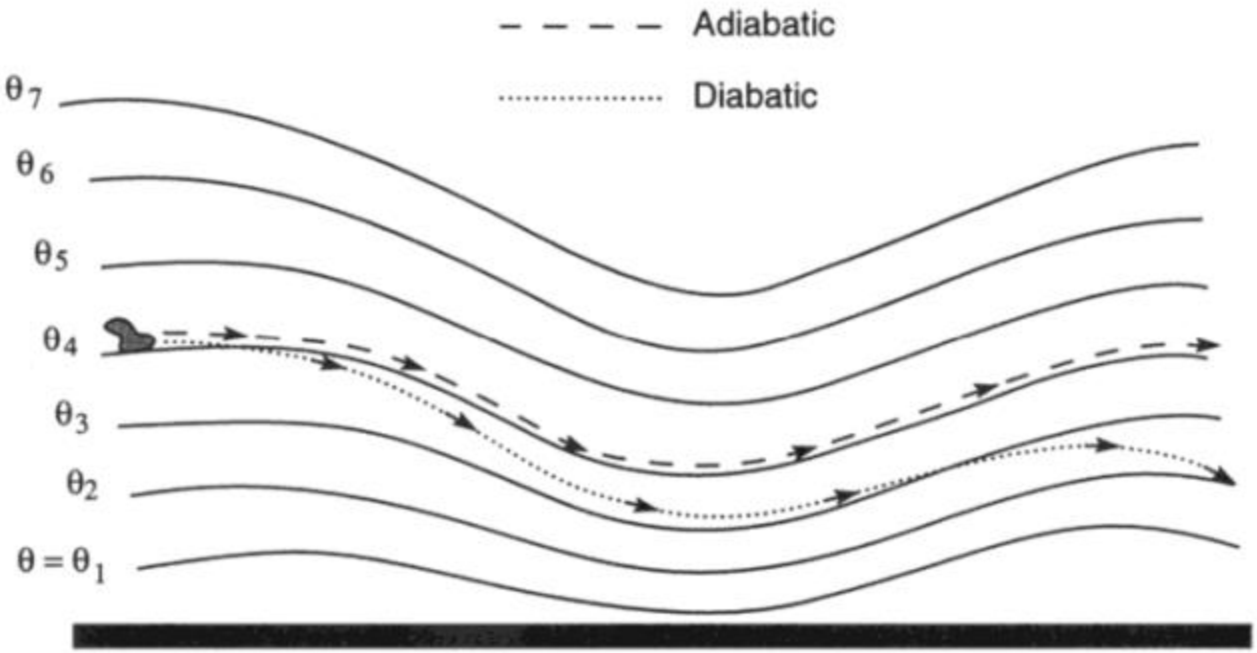
It also excludes irreversible expansion work because such work introduces internal motions that eventually results in mixing.

The conditions for adiabatic behavior are equivalent to conditions for isentropic behavior $\rightarrow$ potential temperature surfaces, θ=const, coincide with isentropic surfaces, s=const.

An air parcel coincident initially with a certain isentropic surface remains on that surface.

Because those surfaces tend to be quasi-horizontal, adiabatic behavior implies no vertical motion.

An air parcels can ascend and descend along isentropic surfaces, but they undergo no systematic vertical motion.



Under diabatic conditions, an air parcel moves across isentropic surfaces according to the heat exchanged with its environment.

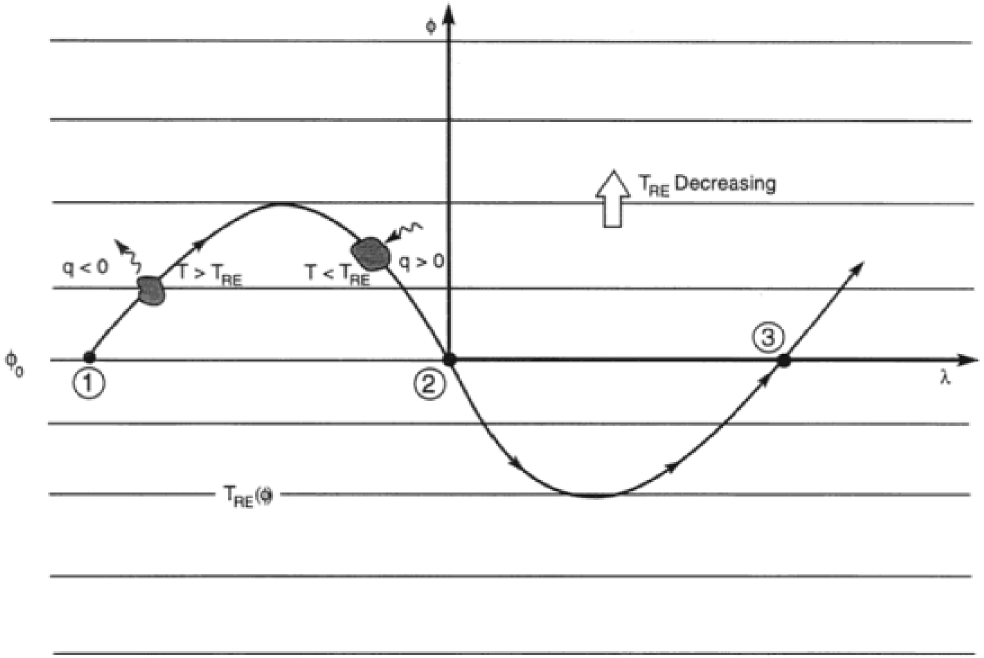
$$d\ln\theta = \frac{\delta q}{c_p T}$$

Consider an air parcel advected horizontally through different thermal environments (e.g. north-south direction).

The figure shows a wavy trajectory followed by an air parcel that is initially at latitude ϕ_0.

The radiative-equilibrium temperature $T_{RE}(\Phi)$ reflects the equilibrium between emission of radiant energy and absorption.

That thermal structure is achieved if the motion is everywhere parallel to latitude circles, because air parcels then have infinite time to ajust to local thermal equilibrium.



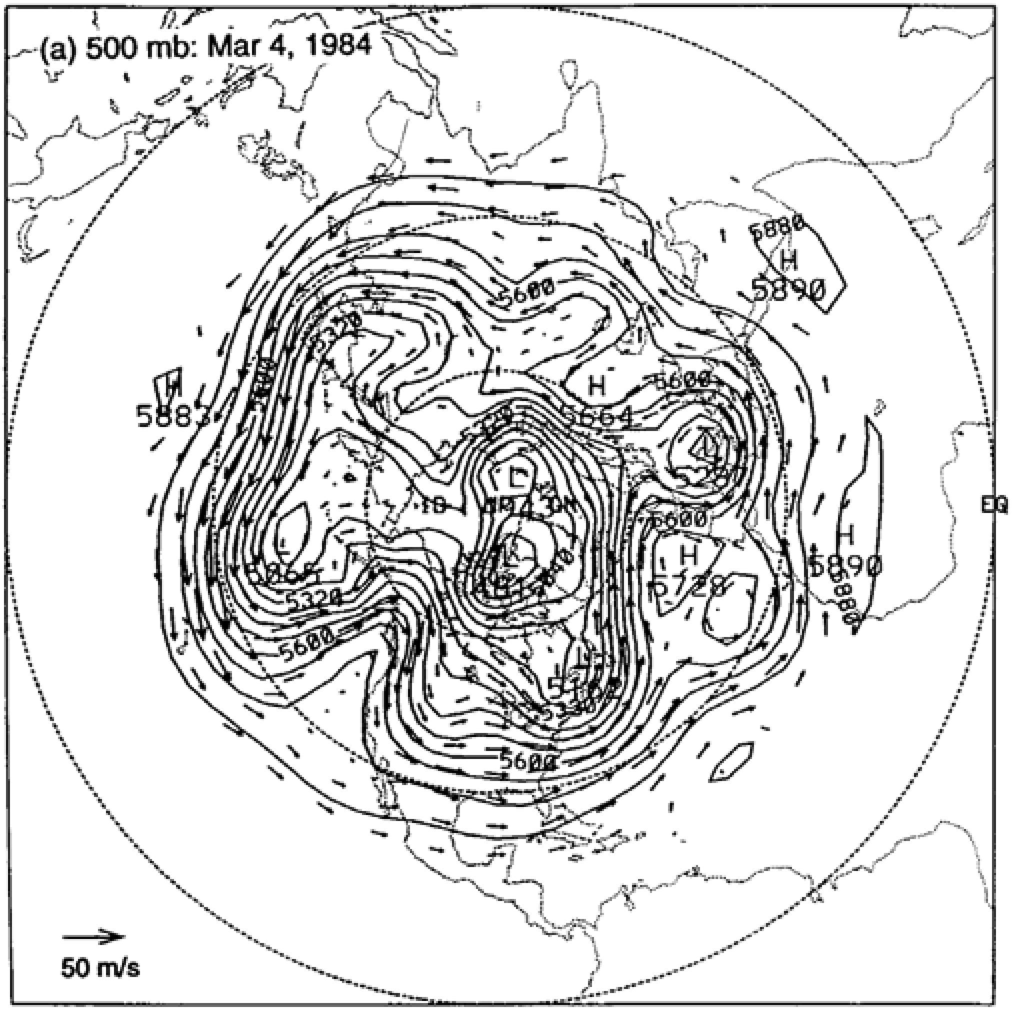


Figure 1.9 (a) Height (contours) of and horizontal velocity (vectors) on the 500-mb isobaric surface for March 4, 1984. (*continues*)

Height (contours) and horizontal velocity (vectors) on the 500-mb isobaric surface for March 4, 1984. (Salby)

Supose the displaced motion is sufficiently slow for the parcel to equilibrate with its surrounding at each point along the trajectory.

The parcel's temperature then differs from T_{RE} only infinitesimally, so the parcel remains in thermal equilibrium and heat transfer along the trajectory occurs reversibly.

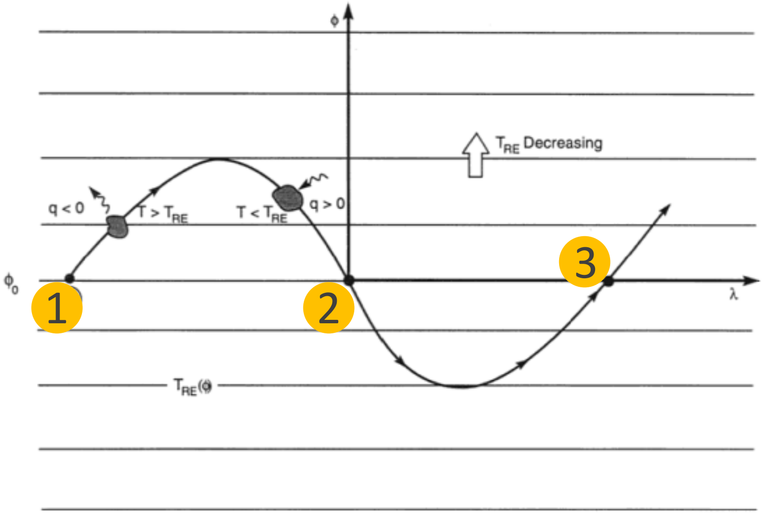
Between two successive crossings of the latitude ϕ_0, the parcel absorbs heat such that

$$\int_1^2 c_p d\ln\theta = \int_1^2 \frac{\delta q}{T}$$

If the heat exchange depends only on the parcel's temperature, for example

$$\delta q = T df(T)$$

$$c_p \ln\left(\frac{\theta_2}{\theta_1}\right) = \Delta f = 0 \quad \text{because} \quad T_1 = T_2 = T_{RE}(\Phi_o)$$



Thus, $\theta_1=\theta_2$ i and the parcel is restored to its initial thermodynamic state when it returns to latitude Φ_0.

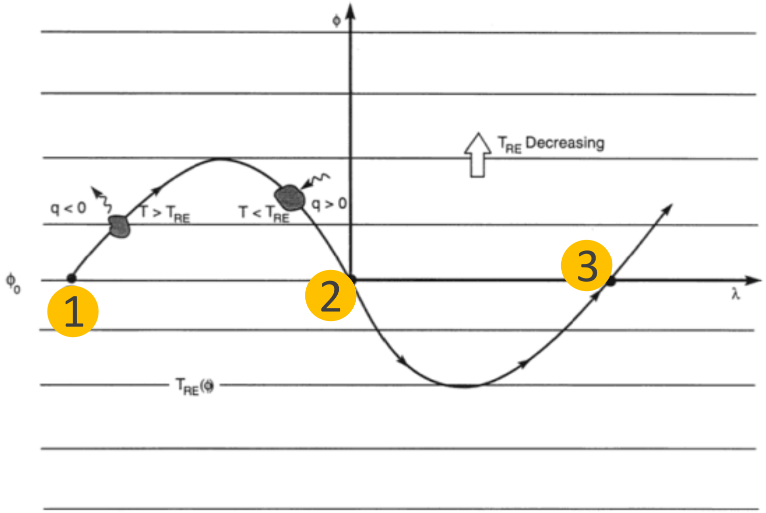
While moving poleward, the parcel is infinitesimally warmer than the local radiative-equilibrium temperature, so its emits more radiant energy than it absorbs.

Rejection of heat results in the parcel drifting off its initial isentropic surface toward lower θ, which corresponds to lower altitude.

While moving equatorward, the parcel is infinitesimally colder than the local radiative-equilibrium temperature, so it absorbs more radiant energy than it emits.

Absorbtion of heat then results in the parcel ascending to higher θ, just enough to restore the parcel to its initial isentropic surface when it returns to the latitude ϕ_0.

Successive crossings of the latitude ϕ_0 result in no vertical motion and the parcel's evolution is perfectly cyclic.

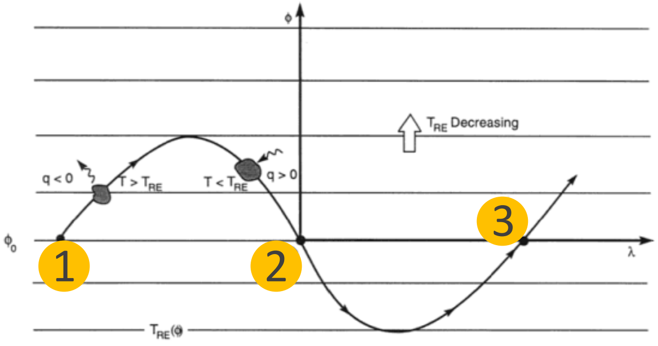


Suppose the motion is sufficiently fast to carry the parcel between radiative environments before it has equilibrated to the local radiative-equilibrium temperature.

During the excursion poleward of ϕ_0, the parcel is out of the thermal equilibrium, so heat transfer along the trajectory occurs irreversibly. Because its temperature lags that of its surroundings, the parcel returns to the latitude ϕ_0 with a temperature different from that initially: $T_1 \neq T_2$.

$$\int_1^2 c_p \mathrm{d}\ln\theta = \int_1^2 \frac{\delta q}{T} \qquad \delta q = T df(T)$$

$$c_p \ln\left(\frac{\theta_2}{\theta_1}\right) = \Delta f \neq 0$$



The parcel's potential temperature also differs from that initially.

The parcel is not restored to its initial isentropic surface, but rather remains displaced vertically after returning to the latitude ϕ_0 .

Whether the parcel returns above or below the initial isentropic surface depends on the radiative-equilibrium temperature and on details of the motion, which control the history of heating and cooling.