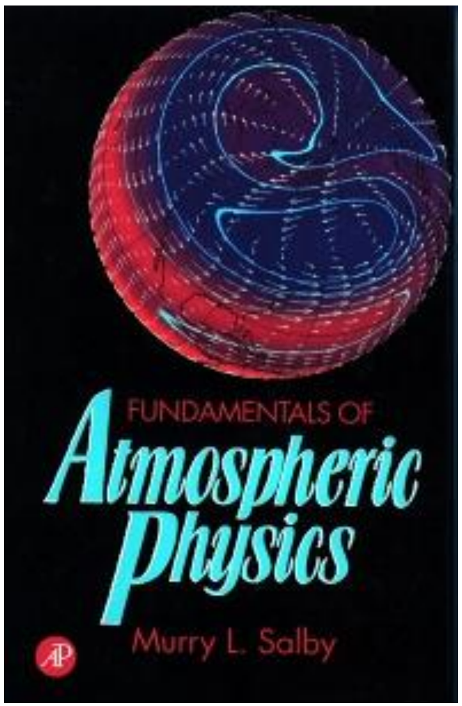
LECTURE OUTLINE

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

UNIVERSITY OF WARSAW

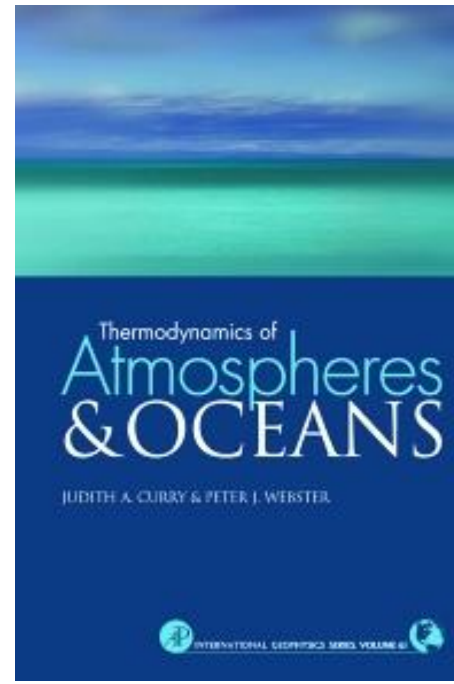
Salby, Chapter 2 and 3



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

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

LECTURE OUTLINE

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

UNIVERSITY OF WARSAW

Second Law of Thermodynamics

The second law of thermodynamics prohibits certain processes, including some in which energy is conserved.

It can be formulated in several equivalent ways.

The entropy statement of the second law is:

There exists an additive state function, known as the **equilibrium entropy**, that never decreases in a thermally isolated system.

$$ds \geq \frac{\delta q}{T}$$

This relation is referred to as the Clausius inequality.

The equality holds if the process is reversible.

For an adiabatic process ($\delta q = 0$) $ds \geq 0$, so the entropy can only increase.

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

The Clausius inequality $ds \geq \frac{\delta q}{T}$ (or $\delta q \leq Tds$) implies that for a given entropy change ds, the maximum heat transfer occurs in a reversible process, for which $\delta q_{rev} = Tds$.

By means of the Clausius inequality $ds \geq \frac{\delta q}{T}$ second law determines whether a system is capable of evolving along a given thermodynamic path.

- $\delta q = Tds \longrightarrow$ reversible process
- $\delta q < Tds \longrightarrow$ irreversible proces (e.q. a natural process)
- $\delta q > Tds \longrightarrow$ impossible process

By substituting the second law: $ds \geq \frac{\delta q}{T} \quad \Rightarrow \quad \delta q \leq Tds$

into the two forms of the first law:

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

we obtain:

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 and are therefore path-independent.

They hold for both reversible and irreversible processes.

These relations are known as the fundamental relations.

Although universally valid, the fundamental relations are not easily evaluated for irreversible processes.

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

The quantities p and T denote the pressure and temperature of the system and are well defined only in equilibrium (i.e., along reversible paths).

Under irreversible conditions, the relations among these variables take the form of inequalities, in which p and T denote externally imposed values that can be specified.

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

Noncompensated heat transfer

The inequalities in the fundamental relations account for the additional heat rejected to the surroundings as a result of irreversibility.
They can be converted into equalities by introducing the notion of uncompensated heat.

$\delta q' > 0$:

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

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

For irreversible process: $$du = (Tds - \delta q') - pdv$$

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} denote the equilibrium values corresponding to the reversible execution of the process.

The uncompensated heat originates from thermal and mechanical disequilibrium, quantified by the differences $T - T_{rev}$ (thermal disequilibrium) and $p - p_{rev}$ (mechanical disequilbrium).

LECTURE OUTLINE

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

UNIVERSITY OF WARSAW

It is convenient to introduce two new state variables:

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

  $df = -sdT - pdv$

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

  $dg = -sdT + vdp$

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

The variables entering the fundamental relations are not mutually independent.

Because the relations involve only state variables, each can be written as an exact differential: $M(x,y)dx + N(x,y)dy = dz$

which requires equality of the mixed partial derivatives (the integrability condition): $\frac{\partial M}{\partial y} = \frac{\partial N}{\partial x}$

These relations are known as the Maxwell relations

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

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

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

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

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:

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

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:

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

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

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

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

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 an ideal gas the entropy expressions take simpler forms:

$$pv = RT$$

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

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

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

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

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

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

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

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

LECTURE OUTLINE

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

UNIVERSITY OF WARSAW

By defining the direction of thermodynamic processes, the second law determines whether a path out of a given thermodynamic state is possible; it thus characterizes the stability of thermodynamic equilibrium.

Consider a system in a given thermodynamic state. An arbitrary infinitesimal process originating from that state is called a virtual process.

The system is said to be in stable (or true) equilibrium if no virtual process originating from that state is a natural process; that is, if all virtual paths out of the 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. In this case, a small perturbation results in a finite change of state.

If only some virtual processes are natural, the system is said to be in metastable equilibrium. A small perturbation may then either produce or fail to produce a finite change of state, depending on the nature 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.

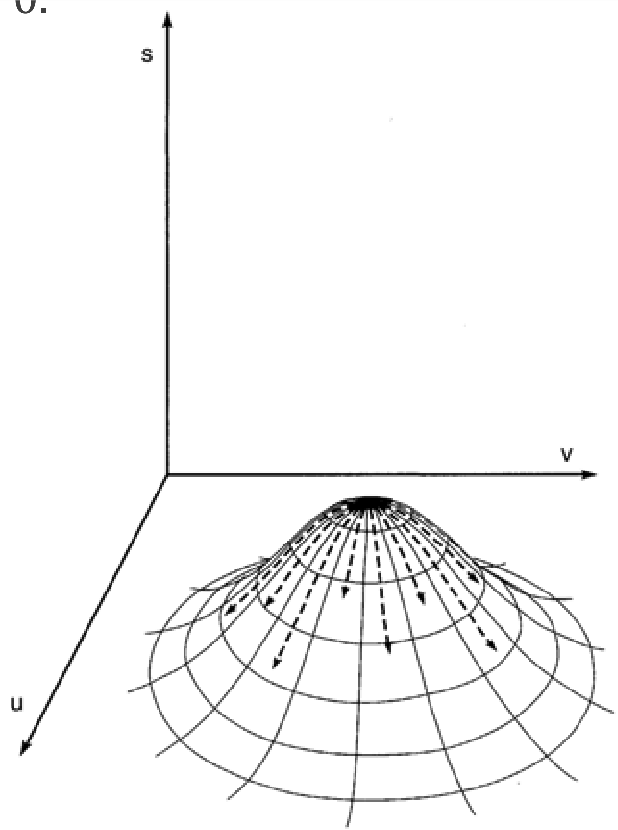
$$du \geq Tds - pdv$$
$$dh \geq Tds + vdp$$
$$df \geq -sdT - pdv$$
$$dg \geq -sdT + vdp$$

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.

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

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

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

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

Implication of Second Law for vertical motion

If a process is adiabatic, $d\theta$=0, and $ds \geq 0$. 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.

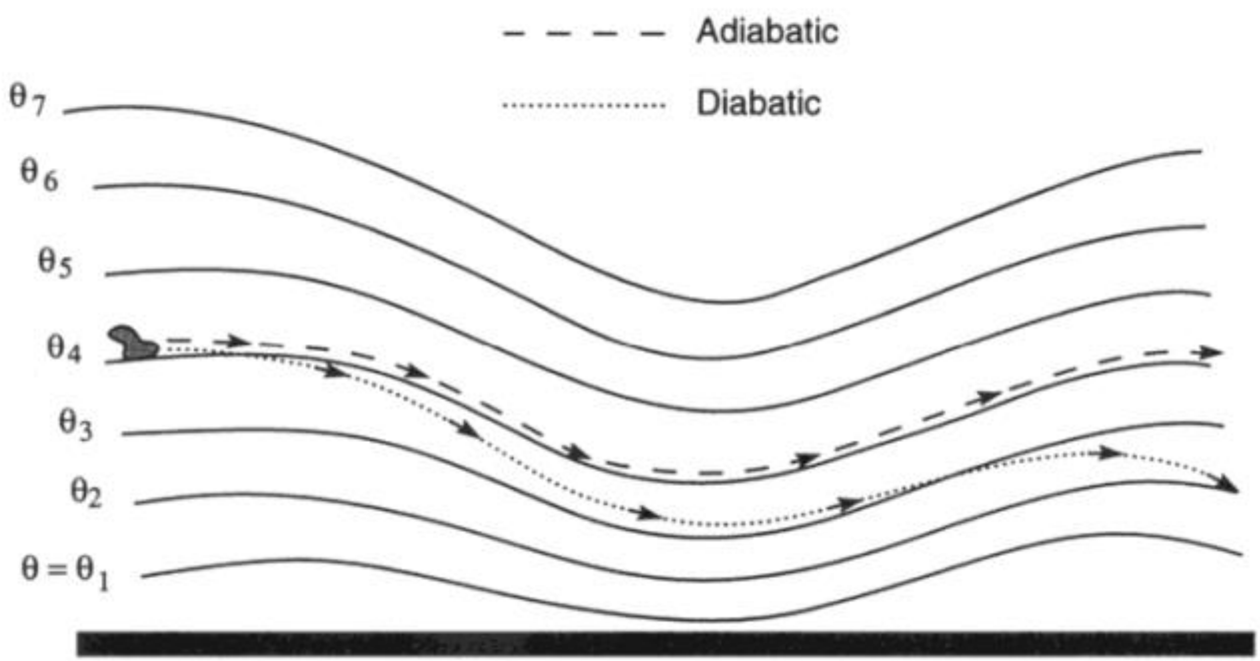
It also excludes irreversible expansion work because such work introduces internal motions that eventually results in mixing.

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.

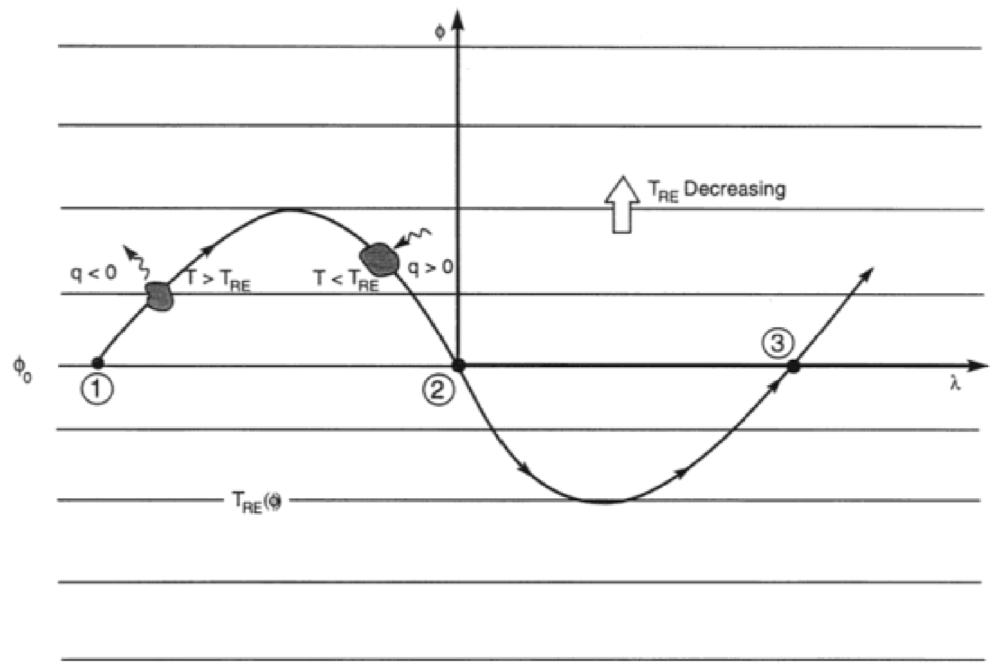
$$d\ln\theta = \frac{\delta q}{c_p T}$$

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.



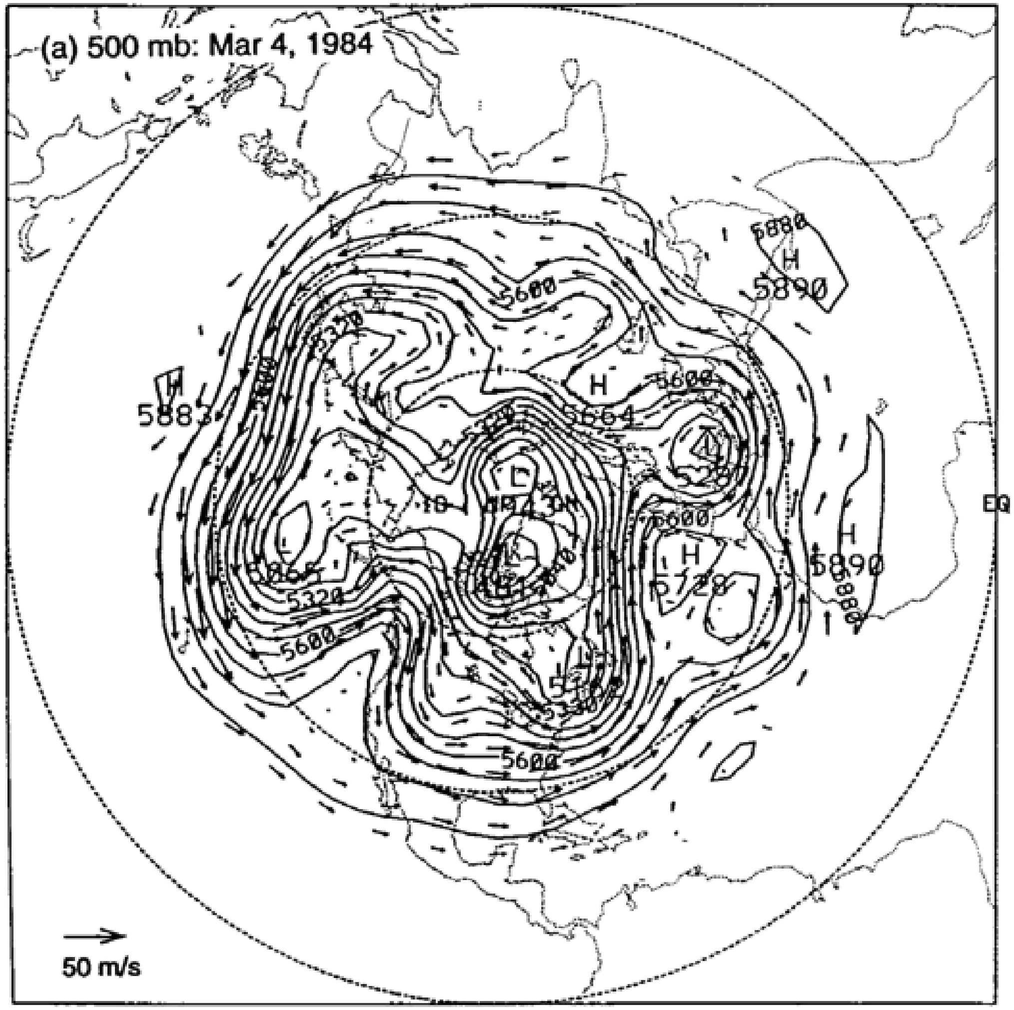


Figure 1.9 (a) Height (contours) of and horizontal velocity (vectors) on the 500-mb isobaric surface for March 4, 1984. (*continues*)

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.

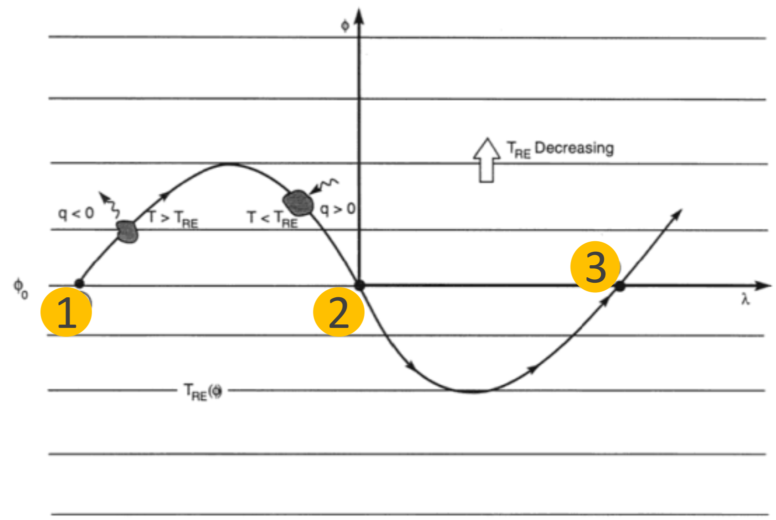
Between two successive crossings of the latitude ϕ_0, the parcel absorbs heat such that

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

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.

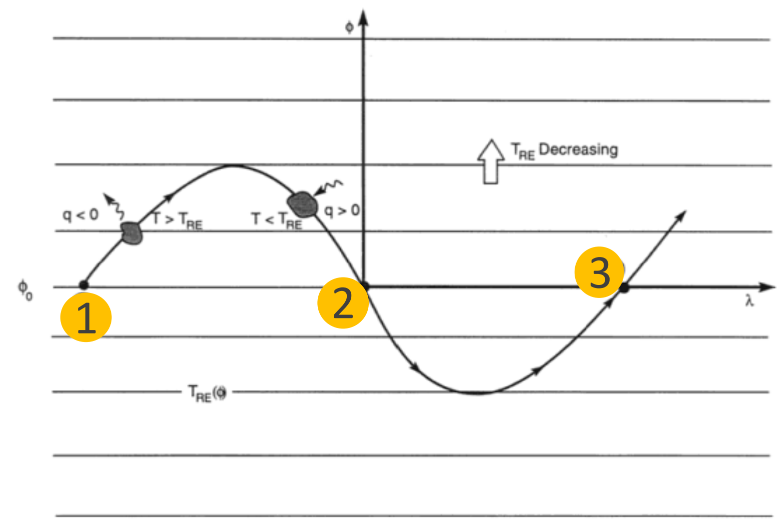
While moving poleward, the parcel is infinitesimally warmer than the local radiative-equilibrium temperature, so its emits more radiant energy than it absorbs.

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.

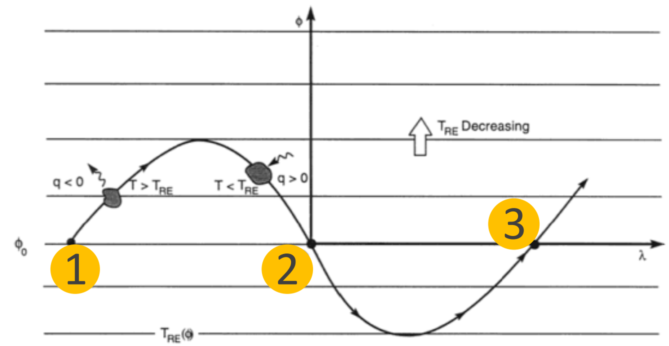
Absorbtion of heat then results in the parcel ascending to higher θ, just enough to restore the parcel to its initial isentropic surface when it returns to the latitude ϕ_0.

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



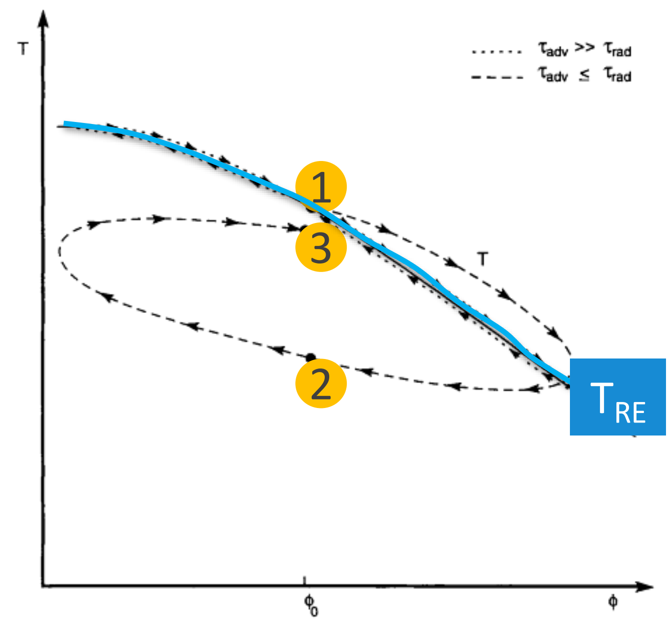
Suppose the motion is sufficiently fast to carry the parcel between radiative environments before it has equilibrated to the local radiative-equilibrium temperature.

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: $T_1 \neq T_2$.



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

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



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.