

# Spring 2012 NNSE 625 Overview

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- **1<sup>st</sup> half of a 1-year integrated course on the fundamental concepts and methods of statistical mechanics, quantum mechanics and their applications to the study of solids, surfaces and nanostructures**
  
- **Instructor: Dr. Y. Alex Xue, Assistant Professor of Nanoscience**
  - Research: Theoretical and computational nanoscience
  - Office: CESTM B230C
  - Office Hour: F 3:30-4:30 PM
  
- **Course Website**
  - <http://www.albany.edu/~yx152122/NNSE625-12.html>
  
- **Study Reading Materials Before AND After Class**
  
- **Course Grading**
  - Distribution: Mid-term paper 20%, Written exam 80%
  - Homework is assigned, collected but not graded.
  - Mid-term paper: A 2-page report on a tutorial article on statistical mechanics
  - Written exam: Comprehensive. Based on home works.
  - Take-home exam: 20% extra credit

# What You Should Know and Where You Can Find Help

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## □ **Introductory quantum mechanics**

- D.J. Griffiths, *Introduction to Quantum Mechanics*
- R. Liboff, *Introductory Quantum Mechanics*
- Foundation of Nanotechnology modules

## □ **Background in thermodynamics**

- Foundation of Nanotechnology modules

## □ **Mathematics**

- Calculus, Linear Algebra, Basic Differential Equations,...
- B.R. Kusse and E.A. Westwig, *Mathematical Physics: Applied Mathematics for Scientists and Engineers*
- M. Abramowitz and I.A. Stegun, *Handbook of Mathematical Functions*
- Matlab/Maple online manual

# Course Topics

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- **Thermodynamics and Statistical Mechanics (Weeks 1-6)**
  1. Fundamentals of Thermodynamics
  2. Thermodynamic Equilibrium and Stability
  3. Probability and Statistics
  4. Statistical Ensemble and Distribution
  
- **Lecture Topics in Quantum mechanics (Weeks 7-12)**
  5. Mathematical Foundation of Quantum Mechanics
  6. Physical Principles of Quantum Mechanics
  7. Spin and Pauli Matrices
  8. Quantum Statistical Mechanics
  9. The Variational Method
  
- **Additional Topics in Quantum Mechanics (Weeks 13-15)**
  10. Stationary Perturbation Theory
  11. Time-Dependent Perturbation Theory
  12. Quantum Theory of Scattering

# Course Texts

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## □ **Statistical Physics**

- 1) D. Chandler, *Introduction to Modern Statistical Mechanics* (Oxford, 1987).
- 2) M. Kardar, *Statistical Physics of Particles* (Cambridge, 2007).
- 3) L.D. Landau and E.M. Lifshitz, *Statistical Physics*, 3rd edition (Elsevier, 1980).

## □ **Quantum Mechanics**

- 1) C. Cohen-Tannoudji et al., *Quantum Mechanics (2 vol. set)*, Wiley-Interscience, 2006.
- 2) P. Atkins and R. Friedman, *Molecular Quantum Mechanics*, 4th edition (Oxford, 2005).
- 3) R. Shankar, *Principles of Quantum Mechanics*, 2nd edition (Plenum Press, 1994).

# Condensed Matter Physics and Nanoscience

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- ☞ Largest subfield of physics
- ☞ Link between atoms and everyday world.
- ☞ Unity obscured by tremendous variety of topics.

☞ Atomic Structure

☞ Electronic Structure

☞ Mechanical Properties

☞ Electron Transport

☞ Optical Properties

☞ Magnetism

☞ Self-organization

☞ Form and Function

☞ Scaling and Symmetry

# Lecture 1. Fundamentals of Thermodynamics

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## □ Fundamental Definitions

**Thermodynamics** is a phenomenological description of properties of macroscopic systems in thermal equilibrium.

- Idealize the system under study as much as possible.
- A **closed** system is an idealization in that it is assumed to be completely isolated by **adiabatic** walls that don't allow any exchange of heat with the surroundings. By contrast, **diathermic** walls allow heat exchange for an **open** system.

# Equilibrium and Thermodynamic Coordinates

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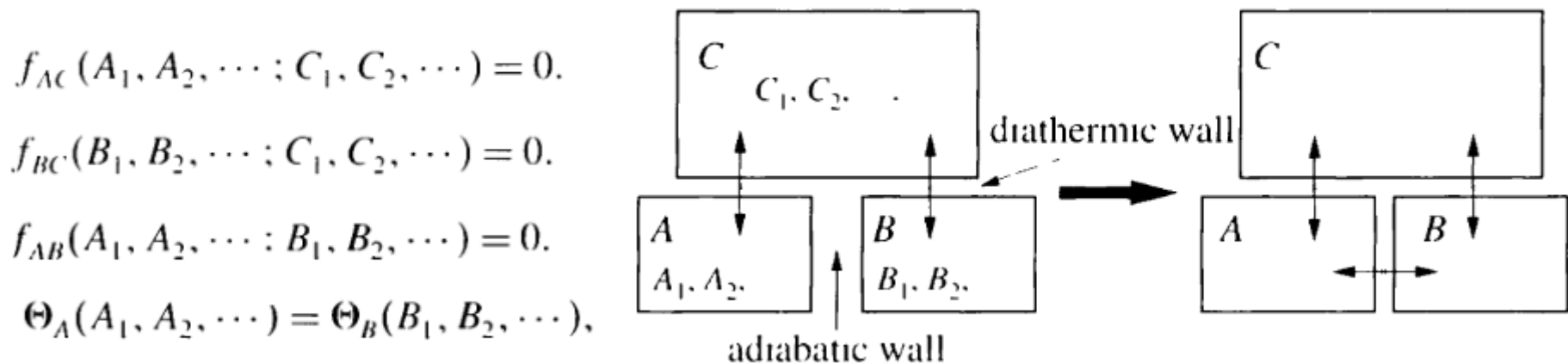
- As the state of a point particle is quantified by its coordinates (and momenta), properties of the macroscopic system can also be described by a number of thermodynamic coordinates or state functions.
- The state functions are well defined only when the system is in equilibrium, that is, when its properties do not change appreciably with time over the intervals of interest (observation times). The dependence on the observation time makes the concept of equilibrium subjective.
- Finally, the relationship between the state functions is described by the laws of thermodynamics. As a phenomenological description, these laws are based on a number of empirical observations.

# The Zeroth Law of Thermodynamics

The zeroth law of thermodynamics describes the transitive nature of thermal equilibrium. It states:

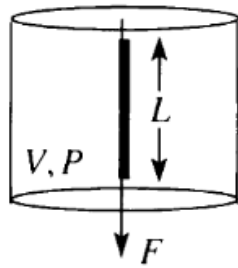
*If two systems, A and B, are separately in equilibrium with a third system, C, then they are also in equilibrium with one another.*

Despite its apparent simplicity, the zeroth law has the consequence of implying the existence of an important state function, the *empirical temperature*  $\Theta$ , such that systems in equilibrium are at the same temperature.

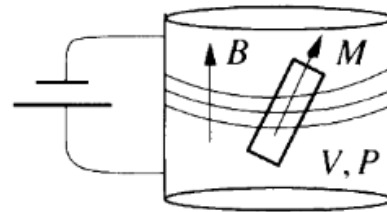


- That is, equilibrium is characterized by a function of thermodynamic coordinates. This function specifies the equation of state

# The Ideal Gas Temperature Scale



(A)&(C)

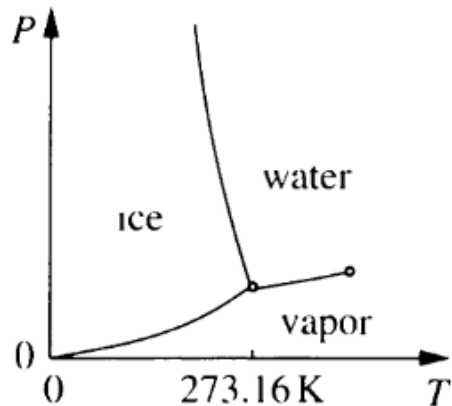


(A)&(B)

**Fig. 1.2** Equilibria of a gas (A) and a magnet (B), and a gas (A) and a wire (C).

$$\begin{aligned} \left(P + \frac{a}{V^2}\right)(V-b)(L-L_0) - c[F - K(L-L_0)] &= 0, \\ \left(P + \frac{a}{V^2}\right)(V-b)M - dB &= 0. \end{aligned} \quad \left\{ \begin{array}{ll} (P + a/V^2)(V-b) = Nk_B T & \text{(van der Waals gas)} \\ M = (N \mu_B^2 B)/(3k_B T) & \text{(Curie paramagnet)} \\ F = (K + DT)(L-L_0) & \text{(Hooke's law for rubber)} \end{array} \right.$$

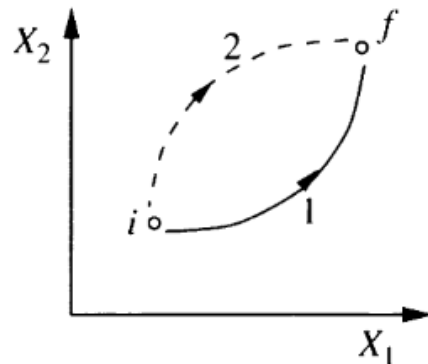
$$\Theta \propto \left(P + \frac{a}{V^2}\right)(V-b) = c \left( \frac{F}{L-L_0} - K \right) = d \frac{B}{M}.$$



$$T(\text{K}) \equiv 273.16 \times \left( \lim_{P \rightarrow 0} (PV)_{\text{system}} / \lim_{P \rightarrow 0} (PV)_{\text{ice-water-gas}} \right).$$

# The First Law of Thermodynamics

*The amount of work required to change the state of an otherwise adiabatically isolated system depends only on the initial and final states, and not on the means by which the work is performed, or on the intermediate stages through which the system passes.*



**Fig. 1.4** The two adiabatic paths for changing macroscopic coordinates between the initial and final point result in the same change in internal energy.

- The first law implies the existence of another state function, the **internal energy  $E(\mathbf{X})$** . It states that both work and heat are forms of energy, and that the total energy is conserved.

$E(\mathbf{X})$  can be obtained from the amount of work  $\Delta W$  needed for an *adiabatic* transformation from an initial state  $\mathbf{X}_i$  to a final state  $\mathbf{X}_f$ , using

$$\Delta W = E(\mathbf{X}_f) - E(\mathbf{X}_i).$$

Another set of observations indicate that once the adiabatic constraint is removed, the amount of work is no longer equal to the change in the internal energy. The difference  $\Delta Q = \Delta E - \Delta W$  is defined as the *heat* intake of the system from its surroundings.

$$\delta Q = dE - \delta W,$$

A *quasi-static* transformation is one that is performed sufficiently slowly so that the system is always in equilibrium.

- The state functions can be divided into a set of **generalized displacements**  $\{x\}$ , and their conjugate **generalized forces**  $\{J\}$ , such that for an infinitesimal quasi-static transformation:  $\delta W = \sum_i J_i dx_i$ .

Table 1.1 *Generalized forces and displacements*

System	Force		Displacement	
Wire	tension	$F$	length	$L$
Film	surface tension	$\mathcal{S}$	area	$A$
Fluid	pressure	$-P$	volume	$V$
Magnet	magnetic field	$H$	magnetization	$M$
Dielectric	electric field	$E$	polarization	$P$
Chemical reaction	chemical potential	$\mu$	particle number	$N$

# Response Functions

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- **Response functions** characterizes and are experimentally measured from the changes of thermodynamic coordinates with external probes.
- **Heat Capacities** measure the change in temperature upon addition of heat to the system. Heat is not a function of state, the path by which it is supplied must also be specified.

$$C_V = \left. \frac{dQ}{dT} \right|_V = \left. \frac{dE - dW}{dT} \right|_V = \left. \frac{dE + PdV}{dT} \right|_V = \left. \frac{\partial E}{\partial T} \right|_V,$$

$$C_P = \left. \frac{dQ}{dT} \right|_P = \left. \frac{dE - dW}{dT} \right|_P = \left. \frac{dE + PdV}{dT} \right|_P = \left. \frac{\partial E}{\partial T} \right|_P + P \left. \frac{\partial V}{\partial T} \right|_P.$$

- **Force Constants** measure the (infinitesimal) ratio of displacement to force and are generalizations of the spring constant.

$$\kappa_T = - \left. \partial V / \partial P \right|_T / V, \quad \chi_T = \left. \partial M / \partial B \right|_T / V.$$

- **Thermal Responses** probe the change in the thermodynamic coordinates with temperature

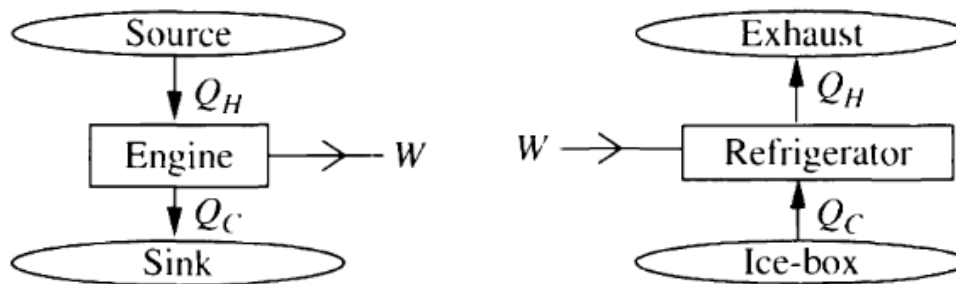
$$\alpha_P = \left. \partial V / \partial T \right|_P / V,$$

# The Second Law of Thermodynamics

**Kelvin's statement.** *No process is possible whose sole result is the complete conversion of heat into work.*

**Clausius's statement.** *No process is possible whose sole result is the transfer of heat from a colder to a hotter body.*

- The second law allows us to construct another important state function, the **entropy  $S$** .



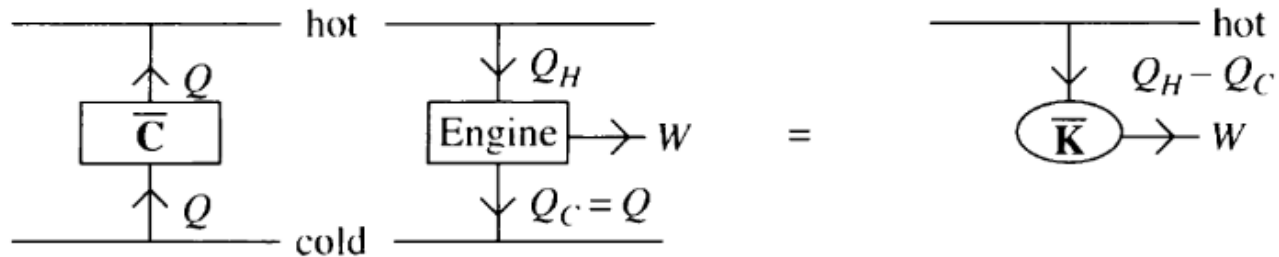
**Fig. 1.6** The idealized engine and refrigerator.

$$\eta = \frac{W}{Q_H} = \frac{Q_H - Q_C}{Q_H} \leq 1.$$

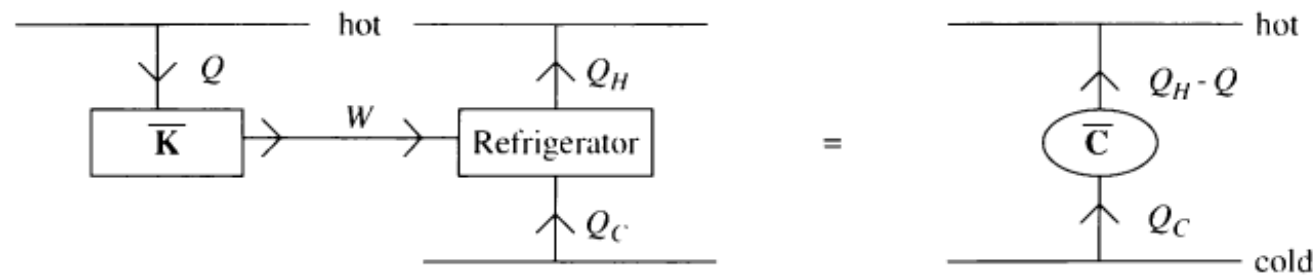
$$\omega = \frac{Q_C}{W} = \frac{Q_C}{Q_H - Q_C}.$$

# Equivalence Between Kelvin's and Clausius's Statements

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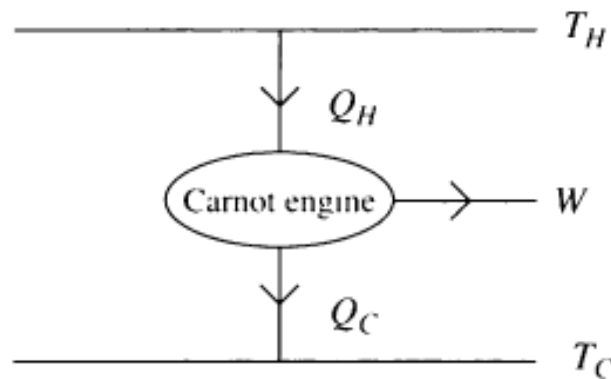
**Fig. 1.7** A machine violating Clausius's statement ( $\bar{C}$ ) can be connected to an engine, resulting in a combined device ( $\bar{K}$ ) that violates Kelvin's statement.



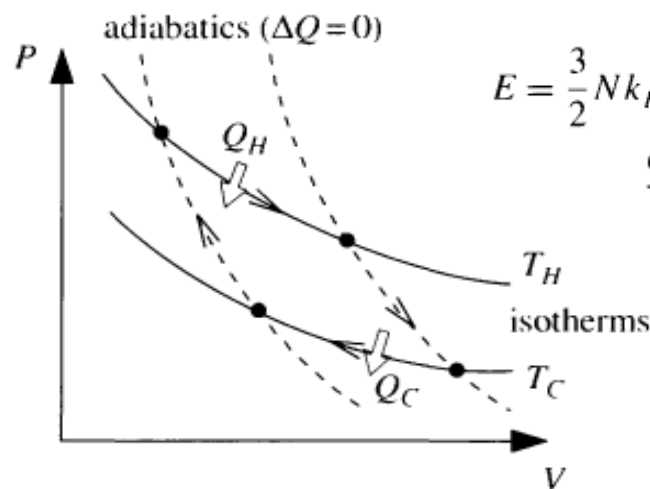
**Fig. 1.8** A machine violating Kelvin's statement can be connected to a refrigerator, resulting in violation of Clausius's statement.

# Carnot Engines and Thermodynamic Temperature

A Carnot engine is any engine that is reversible, runs in a cycle, with all of its heat exchanges taking place at a source temperature  $T_H$ , and a sink temperature  $T_C$ .



**Fig. 1.9** A Carnot engine operates between temperatures  $T_H$  and  $T_C$ , with no other heat exchanges.



$$E = \frac{3}{2} N k_B T = \frac{3}{2} P V. \quad dQ = dE - dW = d\left(\frac{3}{2} P V\right) + P dV = \frac{5}{2} P dV + \frac{3}{2} V dP.$$

$$\frac{dP}{P} + \frac{5}{3} \frac{dV}{V} = 0, \quad \Rightarrow \quad P V^\gamma = \text{constant},$$

**Fig. 1.10** The Carnot cycle for an ideal gas, with isothermal and adiabatic paths indicated by solid and dashed lines, respectively.

# Carnot Engines and Thermodynamic Temperature

**Step 1.** Isothermal expansion from volume  $V_1$  to volume  $V_2$  at constant temperature  $T_h$ . For the isotherm it holds that

$$\frac{V_2}{V_1} = \frac{p_1}{p_2} \quad \Delta Q_1 = -\Delta W_1 = NkT_h \ln \frac{V_2}{V_1}$$

**Step 2.** Adiabatic expansion of the isolated working material from  $V_2$  to  $V_3$ . Here the temperature changes from  $T_h$  to  $T_c$ . The indices  $h$  and  $c$  denote *hot* and *cold*, i.e.,  $T_h > T_c$ :

$$\frac{V_3}{V_2} = \left( \frac{T_h}{T_c} \right)^{3/2}$$

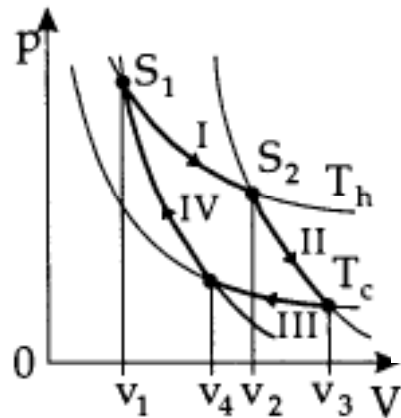
**Step 3.** We now compress the system isothermally from  $V_3$  to  $V_4$  at the (constant) smaller temperature  $T_c$ . Analogously to Step 1 we have

$$\frac{V_4}{V_3} = \frac{p_3}{p_4} \quad \Delta Q_3 = -\Delta W_3 = NkT_c \ln \frac{V_4}{V_3}$$

**Step 4.** Finally we restore the system to the initial state via an adiabatic compression from  $V_4$  to  $V_1$ . The temperature increases again from  $T_c$  to  $T_h$ :

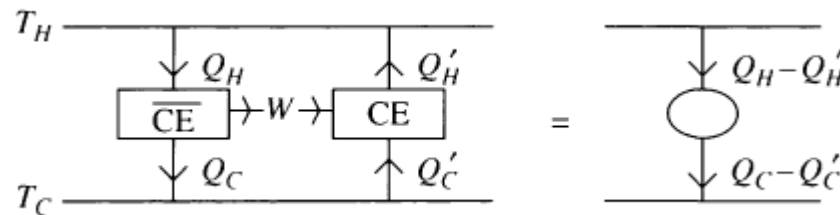
$$\frac{V_1}{V_4} = \left( \frac{T_c}{T_h} \right)^{3/2}$$

$$\frac{\Delta Q_1}{T_h} + \frac{\Delta Q_3}{T_c} = 0 \quad \oint \frac{\delta Q_{\text{rev}}}{T} = 0$$



**Figure 2.1.** Carnot process in the  $pV$  diagram.

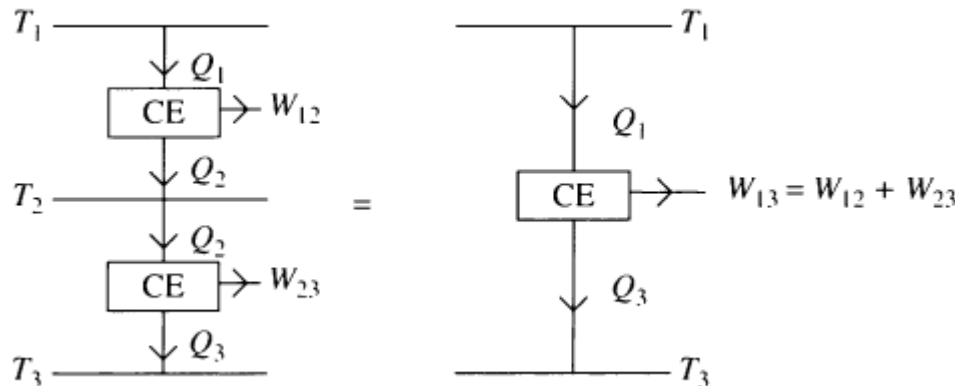
**Carnot's theorem** No engine operating between two reservoirs (at temperatures  $T_H$  and  $T_C$ ) is more efficient than a Carnot engine operating between them.



$$\frac{W}{Q_H} \leq \frac{W}{Q'_H}, \implies \eta_{\text{Carnot}} \geq \eta_{\text{non-Carnot}}$$

**Fig. 1.11** A generic engine is used to run a Carnot engine in reverse.

**Corollary** All reversible (Carnot) engines have the same *universal* efficiency  $\eta(T_H, T_C)$ , since each can be used to run any other one backward.



**Fig. 1.12** Two Carnot engines connected in series are equivalent to a third.

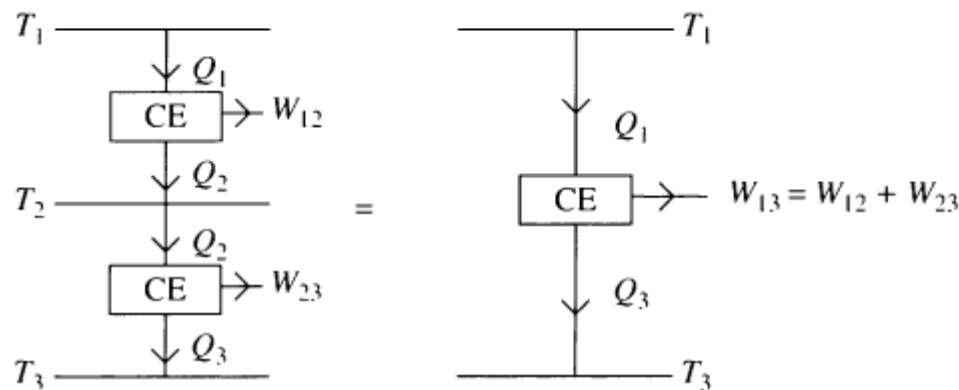
$$[1 - \eta(T_1, T_3)] = [1 - \eta(T_1, T_2)][1 - \eta(T_2, T_3)].$$

$$1 - \eta(T_1, T_2) = \frac{Q_2}{Q_1} \equiv \frac{T_2}{T_1},$$

$$\implies \eta(T_H, T_C) = \frac{T_H - T_C}{T_H}.$$

# The Thermodynamic Temperature Scale

**Corollary** All reversible (Carnot) engines have the same *universal* efficiency  $\eta(T_H, T_C)$ , since each can be used to run any other one backward.



**Fig. 1.12** Two Carnot engines connected in series are equivalent to a third.

$$\begin{cases} Q_2 = Q_1 - W_{12} = Q_1[1 - \eta(T_1, T_2)], \\ Q_3 = Q_2 - W_{23} = Q_2[1 - \eta(T_2, T_3)] = Q_1[1 - \eta(T_1, T_2)][1 - \eta(T_2, T_3)], \\ Q_3 = Q_1 - W_{13} = Q_1[1 - \eta(T_1, T_3)]. \end{cases}$$

$$[1 - \eta(T_1, T_3)] = [1 - \eta(T_1, T_2)][1 - \eta(T_2, T_3)].$$

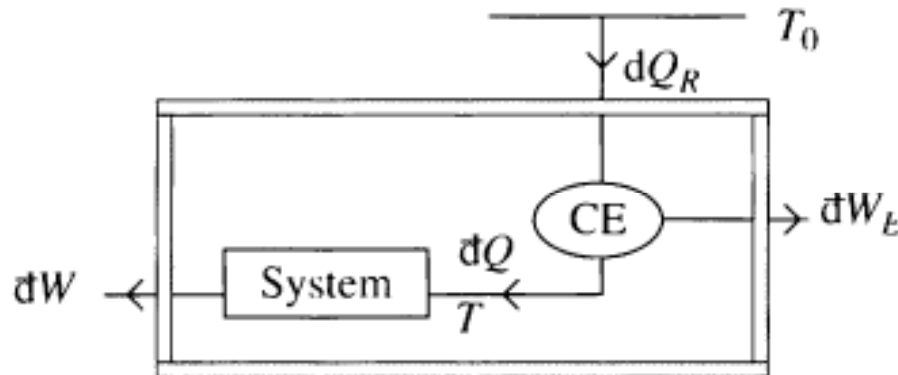
$$1 - \eta(T_1, T_2) = \frac{Q_2}{Q_1} \equiv \frac{T_2}{T_1},$$

$$\Rightarrow \eta(T_H, T_C) = \frac{T_H - T_C}{T_H}.$$

All thermodynamic temperatures are positive,

# Thermodynamic Entropy

**Clausius's theorem** For any cyclic transformation (reversible or not),  $\oint \frac{\delta Q}{T} \leq 0$ , where  $\delta Q$  is the heat increment supplied to the system at temperature  $T$ .



**Fig. 1.13** The heat exchanges of the system are directed to a Carnot engine with a reservoir at  $T_0$ .

$$\delta Q_R = T_0 \frac{\delta Q}{T}. \quad Q_R = W \leq 0,$$

$$T_0 \oint \frac{\delta Q}{T} \leq 0, \quad \Rightarrow \quad \oint \frac{\delta Q}{T} \leq 0,$$

## Consequences of Clausius's Theorem

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1. For a *reversible cycle*  $\oint \mathrm{d}Q_{\text{rev}}/T = 0$ , since by running the cycle in the opposite direction  $\mathrm{d}Q_{\text{rev}} \rightarrow -\mathrm{d}Q_{\text{rev}}$ , and by the above theorem  $\mathrm{d}Q_{\text{rev}}/T$  is both non-negative and non-positive, hence zero. This result implies that the integral of  $\mathrm{d}Q_{\text{rev}}/T$  between any two points  $A$  and  $B$  is independent of path, since for two paths (1) and (2)

$$\int_A^B \frac{\mathrm{d}Q_{\text{rev}}^{(1)}}{T_1} + \int_B^A \frac{\mathrm{d}Q_{\text{rev}}^{(2)}}{T_2} = 0, \quad \implies \int_A^B \frac{\mathrm{d}Q_{\text{rev}}^{(1)}}{T_1} = \int_A^B \frac{\mathrm{d}Q_{\text{rev}}^{(2)}}{T_2}. \quad (1.25)$$

2. Using Eq. (1.25) we can construct yet another function of state, the *entropy*  $S$ . Since the integral is independent of path, and only depends on the two end-points, we can set

$$S(B) - S(A) \equiv \int_A^B \frac{\mathrm{d}Q_{\text{rev}}}{T}. \quad (1.26)$$

For reversible processes, we can now compute the heat from  $\mathrm{d}Q_{\text{rev}} = T\mathrm{d}S$ . This allows us to construct adiabatic curves for a general (multivariable) system from the condition of constant  $S$ . Note that Eq. (1.26) only defines the entropy up to an overall constant.

3. For a reversible (hence quasi-static) transformation,  $\delta Q = TdS$  and  $\delta W = \sum_i J_i dx_i$ , and the first law implies

$$dE = \delta Q + \delta W = TdS + \sum_i J_i dx_i. \quad (1.27)$$

We can see that in this equation  $S$  and  $T$  appear as conjugate variables, with  $S$  playing the role of a displacement, and  $T$  as the corresponding force. This identification allows us to make the correspondence between mechanical and thermal exchanges more precise, although we should keep in mind that unlike its mechanical analog, temperature is always positive. While to obtain Eq. (1.27) we had to appeal to reversible transformations, it is important to emphasize that it is a relation between functions of state. Equation (1.27) is likely the most fundamental and useful identity in thermodynamics.

4. The number of *independent variables* necessary to describe a thermodynamic system also follows from Eq. (1.27). If there are  $n$  methods of doing work on a system, represented by  $n$  conjugate pairs  $(J_i, x_i)$ , then  $n + 1$  independent coordinates are necessary to describe the system. (We shall ignore possible constraints between the mechanical coordinates.) For example, choosing  $(E, \{x_i\})$  as coordinates, it follows from Eq. (1.27) that

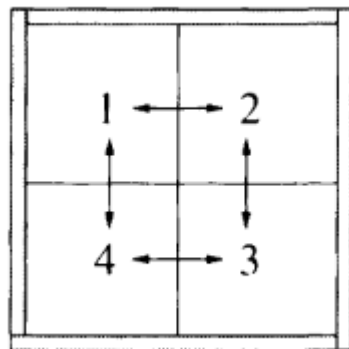
$$\left. \frac{\partial S}{\partial E} \right|_{\mathbf{x}} = \frac{1}{T} \quad \text{and} \quad \left. \frac{\partial S}{\partial x_i} \right|_{E, \{x_j \neq i\}} = -\frac{J_i}{T}. \quad (1.28)$$

( $\mathbf{x}$  and  $\mathbf{J}$  are shorthand notations for the parameter sets  $\{x_i\}$  and  $\{J_i\}$ .)

5. Consider an irreversible change from  $A$  to  $B$ . Make a complete cycle by returning from  $B$  to  $A$  along a reversible path. Then

$$\int_A^B \frac{\delta Q}{T} + \int_B^A \frac{\delta Q_{\text{rev}}}{T} \leq 0, \quad \implies \int_A^B \frac{\delta Q}{T} \leq S(B) - S(A). \quad (1.29)$$

In differential form, this implies that  $dS \geq \delta Q/T$  for any transformation. In particular, consider adiabatically isolating a number of subsystems, each initially separately in equilibrium. As they come to a state of joint equilibrium, since the net  $\delta Q = 0$ , we must have  $\delta S \geq 0$ . Thus an adiabatic system attains a maximum value of entropy in equilibrium since spontaneous internal changes can only increase  $S$ . The direction of increasing entropy thus points out the arrow of time, and the path to equilibrium. The mechanical analog is a point mass placed on a surface, with gravity providing a downward force. As various constraints are removed, the particle will settle down at locations of decreasing height. The statement about the increase of entropy is thus no more mysterious than the observation that objects tend to fall down under gravity!



**Fig. 1.15** The initially isolated subsystems are allowed to interact, resulting in an increase of entropy.

# Principle of Maximal Entropy

There is an extensive function of state,  $S(E, \mathbf{X})$ , which is a monotonically increasing function of  $E$ , and if state  $B$  is adiabatically accessible from state  $A$ , then  $S_B \geq S_A$ .

$$dS = (\partial S / \partial E)_{\mathbf{X}} dE + (\partial S / \partial \mathbf{X})_E \cdot d\mathbf{X},$$

$$T \equiv (\partial E / \partial S)_{\mathbf{X}} \geq 0.$$

$$dS = (1/T) dE - (\mathbf{f}/T) \cdot d\mathbf{X}$$

$$dE = T dS + \mathbf{f} \cdot d\mathbf{X}.$$

$$S(E, \mathbf{X}) > S(E, \mathbf{X}; \text{internal constraint}).$$

In other words, the equilibrium state is the state at which  $S(E, \mathbf{X}; \text{internal constraint})$  has its global maximum.

Internal constraints are constraints that couple to extensive variables but do not alter the total value of those extensive variables.

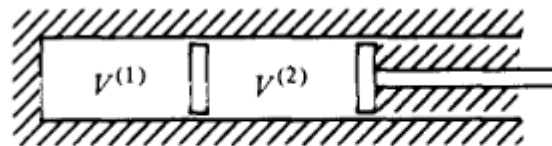


Fig. 1.3. Composite system illustrating the meaning of internal constraints.