

Chapitre 8

Conductivité thermique

La conductivité thermique des gaz

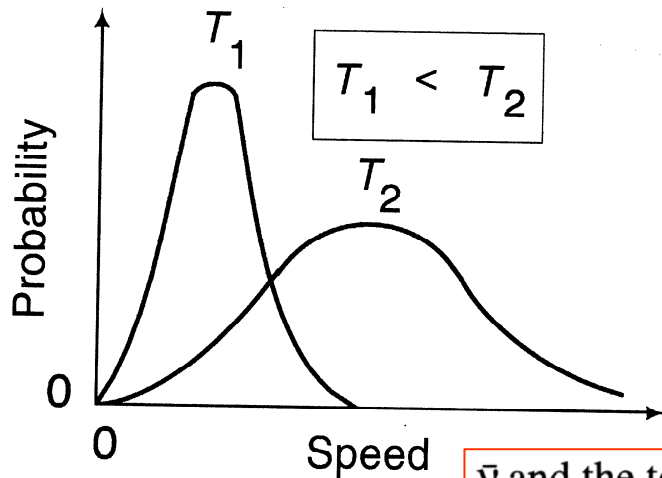


Figure 8.1. Distributions of molecular speeds in a gas at two different temperatures.

Une analyse basée sur la théorie cinétique des gaz

\bar{v} and the temperature of the gas:

$$\bar{v}^2 = \text{const} \times T$$

which follows from consideration of the translational kinetic energy, KE :

$$KE = \frac{1}{2}m\bar{v}^2 = \text{const} \times kT$$

where the latter proportionality comes from equipartition theory (Chapter 6).

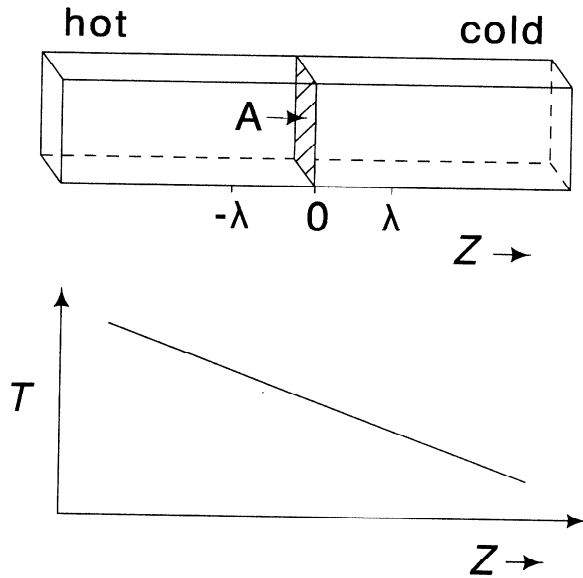


Figure 8.2. A box of gas with a temperature gradient, used to consider the thermal conductivity of a gas. T is the temperature of the gas as a function of position z .

$$J_z(\text{energy}) = -\kappa \left(\frac{dT}{dz} \right) \quad (8.4)$$

Le flux d'énergie J est défini comme la quantité de chaleur écoulee par unité de temps et par unité d'interface (coupe transversale) ($\text{J m}^{-2} \text{s}^{-1} = \text{W m}^{-2}$)

K est le coefficient de conductivité thermique ($\text{J s}^{-1} \text{m}^{-1} \text{K}^{-1}$). On cherche une expression de K en termes des paramètres ayant une signification physique.

La conductivité thermique est une propriété de transport impliquant le mouvement de chaleur (énergie) d'une place chaude à une place froide. Un gradient de température est nécessaire.

Autres propriétés de transport: effusion, diffusion, viscosité, conductivité électrique.

λ : libre parcours moyen

N : densité en nombre de molécules

$$J_z(\text{energy})^{\text{L} \rightarrow \text{R}} = \frac{N\bar{v}}{6} \varepsilon(-\lambda). \quad (8.5)$$

There is also a flux of molecules to A from the right, of $(N\bar{v})/6$, giving right-to-left energy flux, $J_z(\text{energy})^{\text{R} \rightarrow \text{L}}$:

$$J_z(\text{energy})^{\text{R} \rightarrow \text{L}} = \frac{N\bar{v}}{6} \varepsilon(\lambda). \quad (8.6)$$

The net energy flux at A will be the difference between these two fluxes:

$$J_z(\text{energy}) = \frac{1}{6} N\bar{v} [\varepsilon(-\lambda) - \varepsilon(\lambda)] = \frac{1}{6} N\bar{v} \Delta\varepsilon \quad (8.7)$$

where $\Delta\varepsilon$ is the difference in energy per molecule at a distance λ to the left of A (i.e., at $z = -\lambda$) to a distance λ to the right of A (i.e., at $z = \lambda$), i.e., $\Delta\varepsilon = \varepsilon(-\lambda) - \varepsilon(\lambda)$. $\Delta\varepsilon$ can be written in terms of the energy gradient, $d\varepsilon/dz$:

$$\Delta\varepsilon = \left(\frac{d\varepsilon}{dz} \right) \Delta z = - \left(\frac{d\varepsilon}{dz} \right) 2\lambda \quad (8.8)$$

$$J_z(\text{energy}) = -\frac{1}{6}N\bar{v}\left(\frac{d\varepsilon}{dz}\right)2\lambda = -\frac{1}{3}N\bar{v}\lambda\left(\frac{d\varepsilon}{dz}\right).$$

Si E est l'énergie totale par unité de volume:

$$\varepsilon = \frac{E}{N} \qquad \frac{d\varepsilon}{dz} = \frac{1}{N} \frac{dE}{dz}.$$

dE est lié au changement de température:

$$dE = \frac{C_{V,m}n}{V} dT \qquad (8.12)$$

so the energy gradient, dE/dz , can be expressed in terms of the temperature gradient, dT/dz :

$$\frac{dE}{dz} = \frac{C_{V,m}n}{V} \frac{dT}{dz}. \qquad (8.13)$$

Substitution of Equations 8.13 and 8.11 into Equation 8.9 leads to:

$$J_z(\text{energy}) = -\frac{1}{3}\bar{v}\lambda C\left(\frac{dT}{dz}\right) \qquad (8.14)$$

where $C = C_{V,m}n/V$ is the heat capacity per unit volume (SI units of C are $\text{J K}^{-1} \text{m}^{-3}$). Comparison of Equations 8.4 and 8.14 leads to

$$\kappa = \frac{1}{3}C\bar{v}\lambda. \qquad (8.15)$$

$$K = (1/3) C v \lambda$$

La conductivité thermique des gaz est déterminée par 1) la capacité calorifique par unité de volume, 2) la vitesse moyenne des molécules et 3) leur libre parcours moyen.

K est dépendante de la température (déterminée par la dépendance de C , v et λ).

K est indépendante de la pression (compensation des effets sur le nombre des molécules transportant la chaleur et le libre parcours moyen)

$$\lambda = \frac{V}{\sqrt{\pi} d^2 n N_A} \quad d \text{ est le diamètre de molécules}$$

$$\kappa = \frac{1}{3} \bar{v} \frac{V}{\sqrt{2\pi} d^2 n N_A} \frac{n}{V} C_{V,m} = \frac{\bar{v} C_{V,m}}{3\sqrt{2\pi} d^2 N_A}$$

TABLE 8.1.**Thermal Conductivities of Selected Materials at $T = 300\text{ K}$**

Material	$\kappa / (\text{W m}^{-1} \text{K}^{-1})$
Al_2O_3	36.0
Argon (gas)	0.018
Boron	2.76
Copper	398
Diamond	2310
Graphite	2000 along c -axis 9.5 along a -axis
Helium (gas)	0.15
Iodine	0.449
MgO	60.0
Nitrogen (gas)	0.025
Black phosphorus	12.1
White phosphorus	0.235
Sapphire	46
SiO_2 (crystalline)	10.4 along c -axis 6.2 along a -axis
SiO_2 (amorphous)	1.38

La conductivité thermique des solides non-métalliques

Dans les gaz, les molécules portent et transportent la chaleur.

Dans les solides, les vibrations des atomes (lattice wave), phonon, sont porteurs de la chaleur.

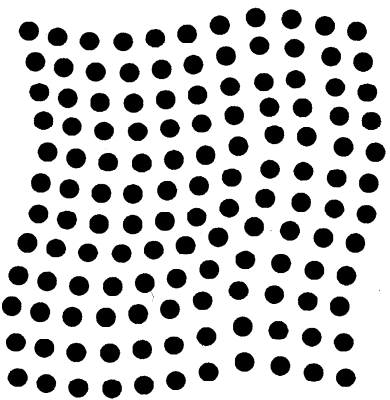


Figure 8.3. Depiction of a lattice wave (phonon) in a two-dimensional solid. At $T = 0$ K, the atoms would be arranged on a regular grid, but this instantaneous picture shows the atoms displaced from their equilibrium positions.

Le phonon est la quantification de l'énergie associée aux vibrations des atomes d'un solide. Il voyage avec la vitesse du son.

$$\kappa = \frac{\dot{q}}{A} \frac{dx}{dT}$$

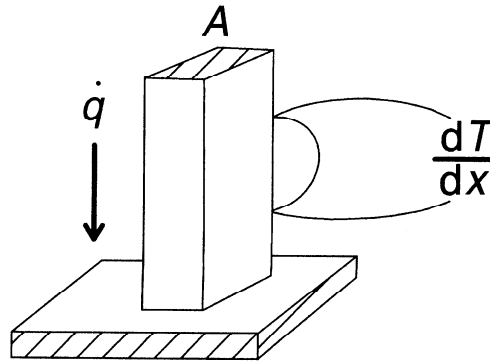


Figure 8.4. The thermal conductivity, κ , of a single crystal (or well-defined block) of a material can be determined by direct measurement. For a crystal of cross-sectional area A , with a temperature gradient along its face of dT/dx , the thermal conductivity is given by $\kappa = \dot{q}(dx/dT)A^{-1}$, where \dot{q} is the power supplied to the top of the crystal. The measurement would be carried out at steady-state conditions, i.e., the rate of power introduced to the top of the crystal would be equal to the loss at the bottom, such that the temperature of the crystal remains constant. In addition, for high-accuracy measurements, care would need to be taken to reduce extraneous heat exchange with the surroundings; for example, the crystal and its platform would be in a vacuum, and the crystal could be surrounded with a temperature-matched heat shield.

$$\kappa_{\text{solid}} = \frac{1}{3} C \bar{v} \lambda$$

C est la capacité calorifique par unité de volume.

\bar{v} et λ sont la vitesse moyenne (vitesse du son $\sim \Theta_D$) et le libre parcours moyen des phonons respectivement.

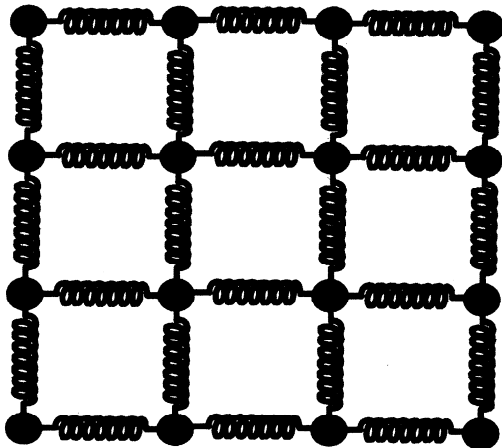


Figure 8.5. A solid can be considered to be a network of atoms, each connected to other atoms by springs.

Quand la température augmente, la probabilité d'exciter les phonons de haute énergie augmente, et plus d'atomes sont déplacés de leurs positions d'équilibre par vibration.

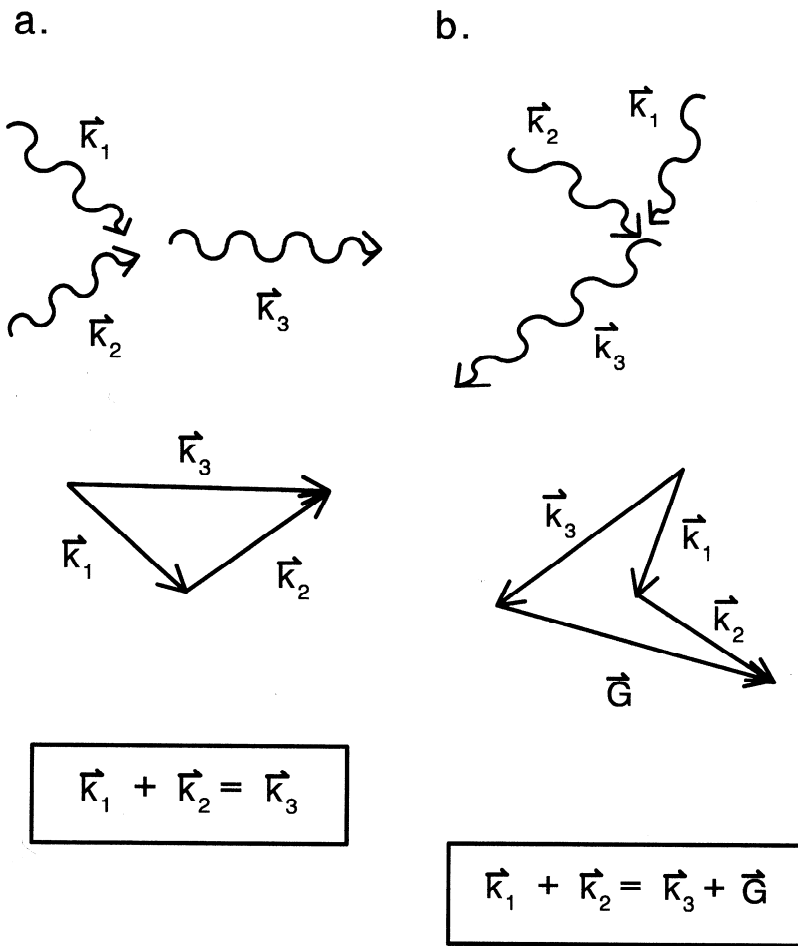


Figure 8.6. (a) Two incident phonons (each shown as a wave) can interact to give a resultant phonon with a motion in the same general direction as the incident phonons. This process is known as a “normal” or “N” process; it does not resist heat flow. The vector view shows \vec{k}_1 and \vec{k}_2 as incident momentum (wave) vectors, and \vec{k}_3 as the resultant wavevector. (b) Two incident phonons (each shown as a wave) can interact to give a resultant phonon with one component of the motion in a direction opposite to the general motion of the incident phonons. This process, since it “turns back” heat flow, is known as an “Umklapp” process. It is these sorts of processes that lead to thermal resistance (reducing thermal conductivity). The vector view shows \vec{k}_1 and \vec{k}_2 as incident wavevectors, and \vec{k}_3 is the resultant wavevector. \vec{G} represents a momentum transfer to the lattice.

Les interactions (collisions) des phonons déterminent la résistance à l'écoulement de chaleur.

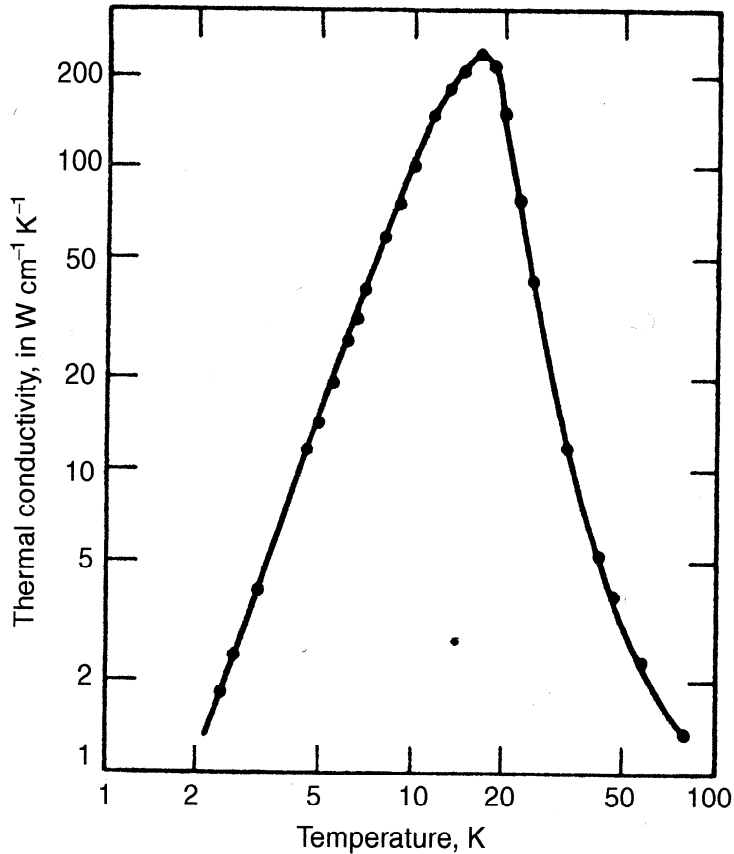


Figure 8.7. The temperature dependence of the thermal conductivity of a “typical” simple insulating crystalline solid, highly purified NaF. From C. Kittel (1995). *Introduction to Solid State Physics*, 7th Ed. Copyright 1995 John Wiley & Sons, Inc. Reprinted by permission of John Wiley & Sons, Inc.

$$\kappa_{\text{solid}} = \frac{1}{3} C \bar{v} \lambda$$

$T > \Theta_D$ (température caractéristique de Debye), C et \bar{v} sont approximativement indépendantes de T , alors que λ diminue quand T augmente à cause de plus de collisions entre les phonons. Conséquemment, K diminue quand T augmente.

$T < \Theta_D$, C diminue quand T abaisse; λ n’augmente plus (limité par la taille du cristal ou les défauts), et \bar{v} reste indépendante de T . Conséquemment, K diminue quand T diminue.

La conductivité thermique des métaux

Il y a deux mécanismes pour la conduction thermique: par phonons et par électrons libres. Le fait que les métaux sont de meilleurs conducteurs thermiques que les solides non-métalliques (κ est de 10-100 fois plus grande) indique que la plupart de chaleur est portée par les électrons libres.

$$\kappa = \kappa_{\text{phonon}} + \kappa_{\text{elec}} \quad (8.20)$$

where κ_{phonon} is as given by Equation 8.19 and, by analogy with Equation 8.15, κ_{elec} is given by

$$\kappa_{\text{elec}} = \frac{1}{3} C_{\text{elec}} \bar{v}_{\text{elec}} \lambda_{\text{elec}} \quad (8.21)$$

where C_{elec} is the electronic contribution to the heat capacity per unit volume, \bar{v}_{elec} is the mean

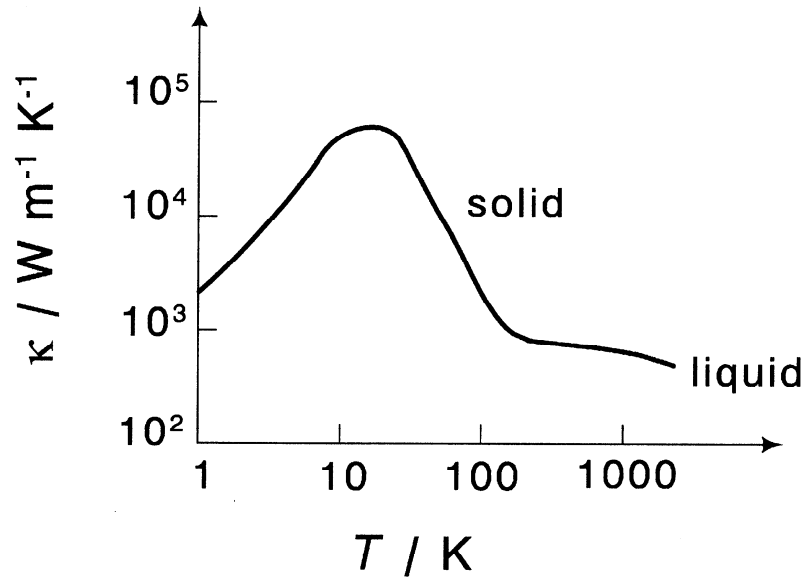


Figure 8.8. Temperature dependence of the thermal conductivity of a “typical” metal. The data shown are for Cu.

Effets similaires de la température sur la conductivité thermique.

Chapitre 9

Stabilité thermique: aspects thermodynamiques

La stabilité thermique d'un matériau (transformations de phases, dégradation) est importante pour déterminer l'usage de ce matériau.

Différents systèmes de matériaux, avec un, deux et trois composants, seront étudiés dans ce chapitre.

Les gaz purs

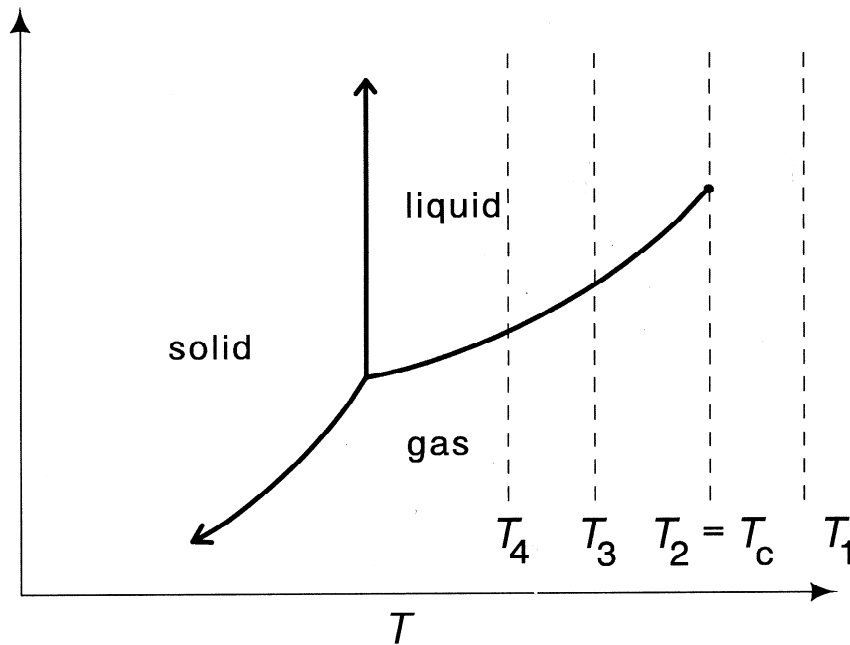


Figure 9.1. The generalized phase diagram for a pure material as a function of temperature (T) and pressure (P). The dashed lines correspond to constant-temperature lines (isotherms) considered further in Figure 9.2.

T_c est la température critique à laquelle la phase liquide ne peut plus être distinguée de la phase gazeuse.

Équilibre entre les phases: Équation de Clapeyron

La phase α est en équilibre avec la phase β aux conditions initiales:

$$G_{\text{initial}}^{\alpha} = G_{\text{initial}}^{\beta} \quad (9.1)$$

and the temperature and pressure are changed (changing G by dG) to final conditions such that the equilibrium of phases α and β is maintained, then

$$G_{\text{final}}^{\alpha} = G_{\text{final}}^{\beta} \quad (9.2)$$

Since

$$G_{\text{final}}^{\alpha} = G_{\text{initial}}^{\alpha} + dG^{\alpha} \quad (9.3)$$

and

$$G_{\text{final}}^{\beta} = G_{\text{initial}}^{\beta} + dG^{\beta} \quad (9.4)$$

it follows that

$$dG^{\alpha} = dG^{\beta} \quad (9.5)$$

$$dG^\alpha = V^\alpha dP - S^\alpha dT = dG^\beta = V^\beta dP - S^\beta dT. \quad (9.6)$$

This can be rearranged to give the quantity we were aiming for, dP/dT :

$$\frac{dP}{dT} = \frac{S^\alpha - S^\beta}{V^\alpha - V^\beta} = \frac{\Delta_{\text{trs}} S}{\Delta_{\text{trs}} V} = \frac{\Delta_{\text{trs}} H}{T \Delta_{\text{trs}} V} \quad (9.7)$$

where the second equality uses the general form of the transition entropy change ($\Delta_{\text{trs}} S$) and transition volume change ($\Delta_{\text{trs}} V$), and the third equality makes use of the generalization

$$\Delta G = \Delta H - T \Delta S \quad (9.8)$$

where, due to the equality of G for any two phases in equilibrium,

$$\Delta_{\text{trs}} G = 0. \quad (9.9)$$

L'équation de Clapeyron (équation 9.7) s'applique à toutes les transitions de phase de premier ordre.

$$\left(\frac{dP}{dT} \right)_{\text{sol-vap}} = \frac{\Delta_{\text{subl}} H}{T \Delta_{\text{subl}} V}$$

$$\left(\frac{dP}{dT} \right)_{\text{sol-liq}} = \frac{\Delta_{\text{fus}} H}{T \Delta_{\text{fus}} V}.$$

Diagrammes de phase des matériaux purs (divers exemples représentatifs)

1. CO₂

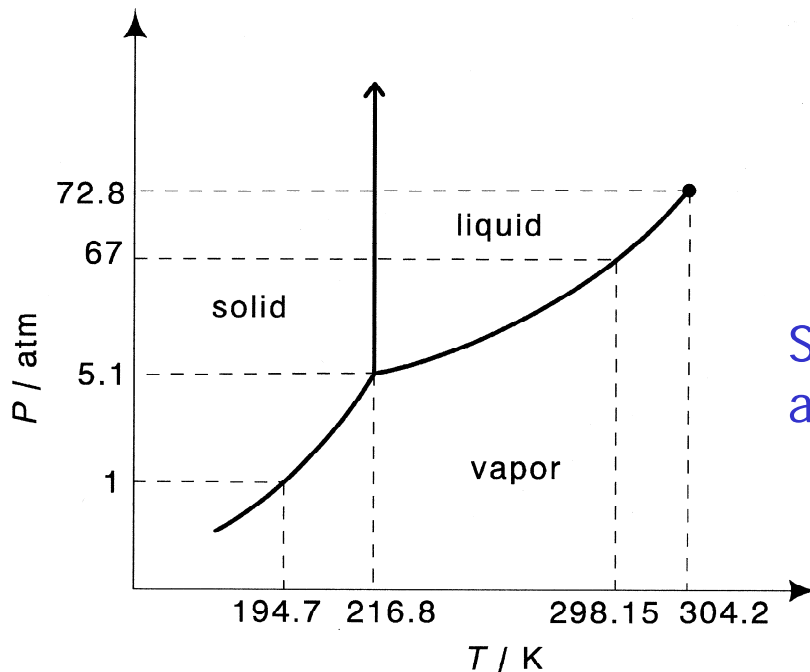


Figure 9.3. The pressure–temperature phase diagram for pure CO₂. The scales are not linear.

Sublimation à pression et température ambiantes – glace sèche

Le fluide supercritique est relativement facile à obtenir et peut être utilisé comme solvants ou agent transporteur (application croissante dans l'industrie)

2. Le soufre

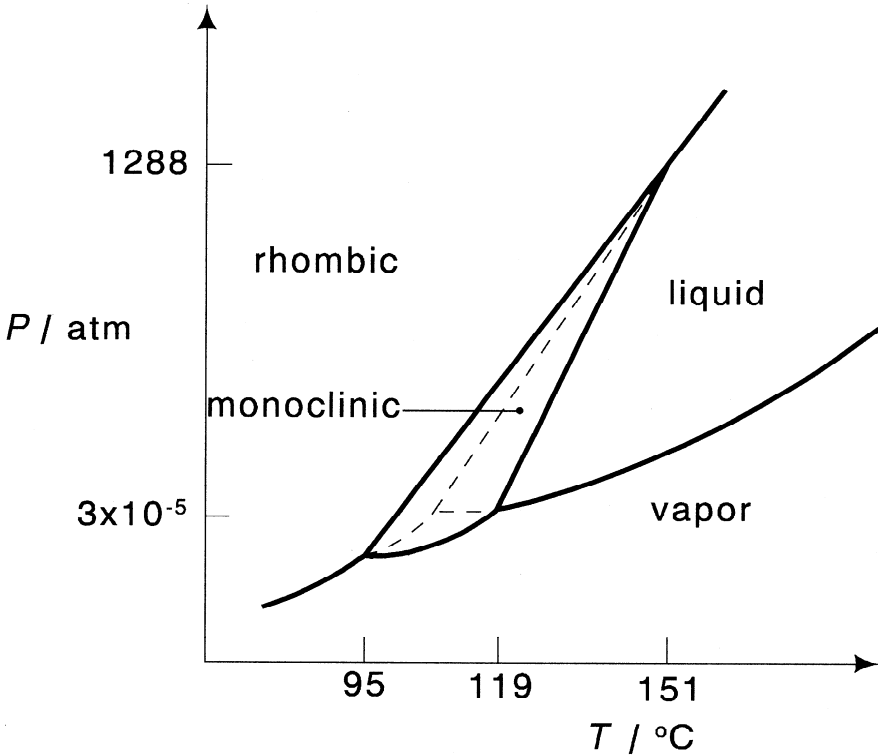


Figure 9.4. The pressure-temperature phase diagram for sulfur. The solid lines indicate the stable phases, and the dashed lines indicate metastability.

Il y a 2 phases solides de différentes structures cristallines - polymorphisme

Une transformation liquide–orthorhombique sans la forme monoclinique est possible. Dans ce cas, le liquide ou le cristal rhombique est métastable à certaines pressions et températures.

3. H₂O

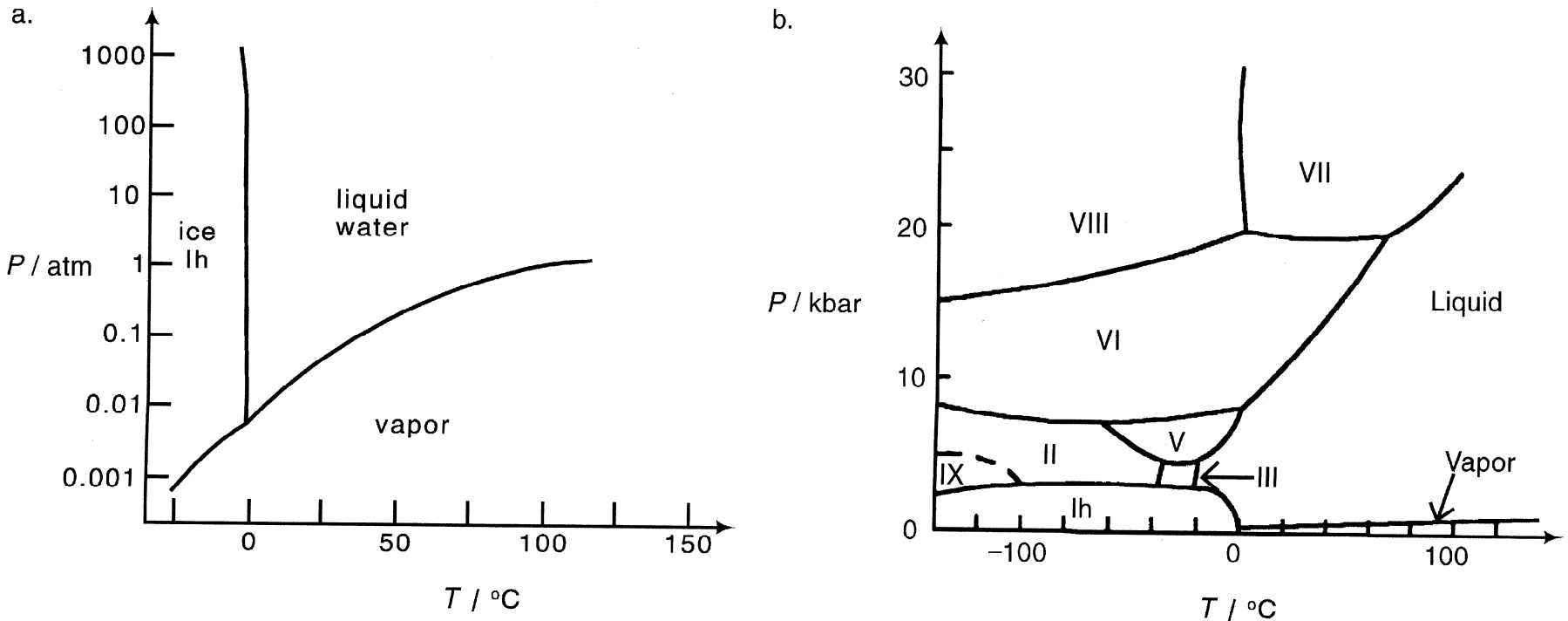


Figure 9.5. The pressure–temperature phase diagram of H₂O (a) at low pressure (note the negative P – T slope) and (b) over a wider pressure range (1 kbar \approx 1000 atm).

Pente négative de la ligne P - T solide-liquide pour la glace Ih ayant une structure cristalline hexagonale ouverte (solide moins dense que liquide)

Polymorphisme à hautes pressions – différentes façons d'arrangement de molécules établissant les ponts d'hydrogène et conduisant à G la plus basse.

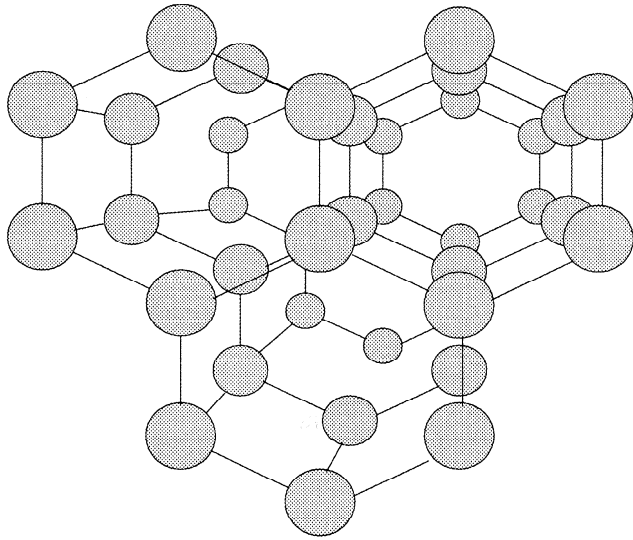


Figure 9.6. The oxygen positions in the hexagonal structure of ice Ih. The hydrogens are not shown because they are disordered. The very open structure makes ice Ih float in liquid water.

La structure hexagonale de la glace à basses pressions

4. Le méthane (CH₄)

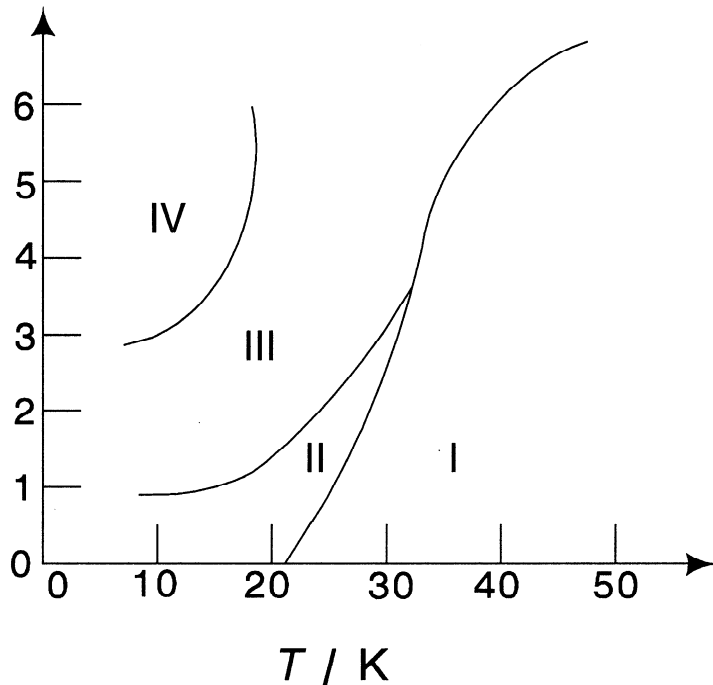


Figure 9.7. The low-temperature phase diagram of CH₄, showing only the solid phases.

Il y a au moins 4 phases solides.

Le polymorphisme est attribué à la forme moléculaire qui est presque sphérique selon la distribution de la densité électronique, ce qui fait que la molécule est facile à tourner.

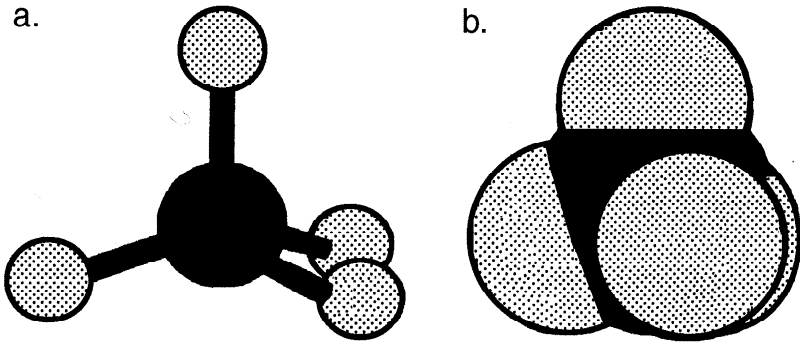


Figure 9.8. Two views of the CH_4 molecule. (a) The ball-and-stick model is useful, but does not truly represent the space-filling shape of the molecule. (b) An electron density distribution view of CH_4 , where there is 95% probability of finding the electrons within the surface shown, shows methane to be a more nearly spherical molecule.

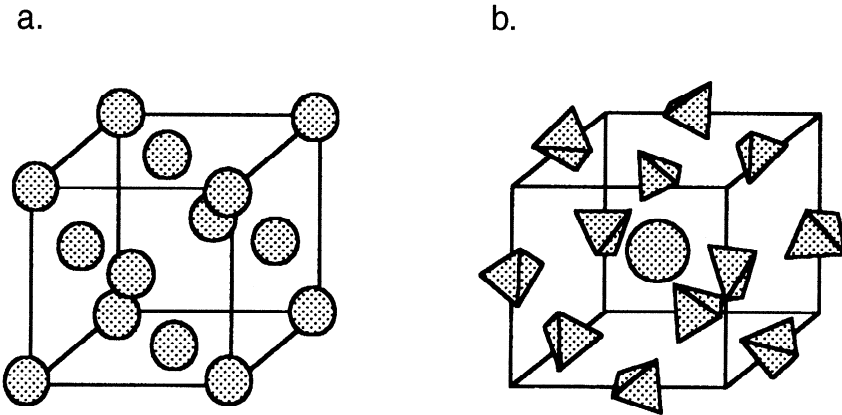


Figure 9.9. Structures of two phases of solid CH_4 . (a) Phase I, with the CH_4 molecules orientationally disordered (shown as spheres to indicate rotating tetrahedra) on sites of a face-centered cubic lattice. (b) Phase II, with some CH_4 molecules orientationally ordered (orientationally ordered tetrahedra) and some experiencing very low (practically zero) barrier to rotation (shown as a sphere in the unit cell). More precisely, the latter molecules are in a spherically symmetric ground state at low temperature.

Une structure peut être ordonnée au niveau de la position des molécules mais désordonnée en termes d'orientations moléculaires.

Un solide désordonné orientationnellement (**cristal plastique**) peut avoir une grande entropie: $S_{\text{liquide}} - S_{\text{solide}} < 20 \text{ J K}^{-1}$

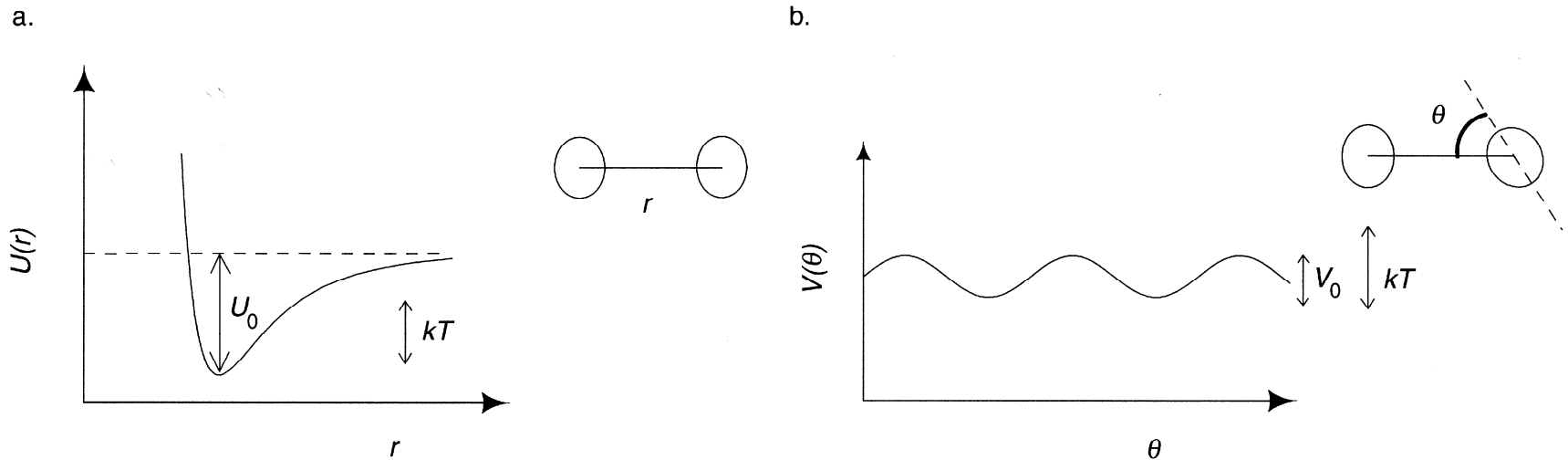


Figure 9.10. The energy of interaction of two nearly spherical molecules that are capable of forming an orientationally disordered solid, as a function of (a) intermolecular separation and (b) angle at fixed separation. If the thermal energy is less than the binding energy [$kT < U_0$ in (a)], the material will be a solid. For a material that can form an orientationally disordered solid, $V_0 \ll U_0$, i.e., the molecules can rotate more easily than they can translate. If the thermal energy (kT) is greater than V_0 , as shown here, the material will be orientationally disordered. At lower temperatures, the stable structure will be that of an ordered solid.

La barrière pour la séparation est beaucoup supérieure à kT , position stable (ordonnée).

La barrière à rotation est plus petite que kT , l'orientation est désordonnée.

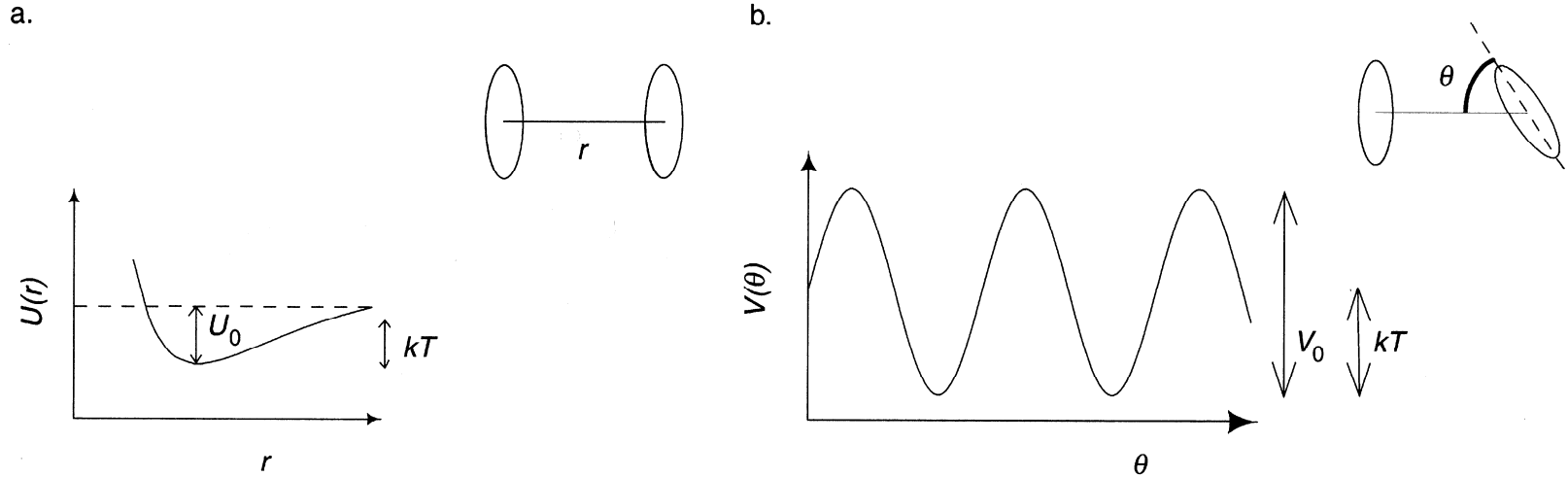


Figure 9.11. The energy of interaction of two rod-shaped molecules that are capable of forming a liquid crystalline phase, as a function of (a) intermolecular separation and (b) angle at fixed separation. For a material that can form a liquid crystal, $U_0 \ll V_0$, i.e., the molecules can translate more easily than they can rotate. If the thermal energy (kT) is nearly equal to U_0 , as shown here, then the material will be liquid crystalline. At lower temperatures, the stable structure will be that of an ordered solid.

La barrière pour la séparation est petite, $\sim kT$, translation facile.

La barrière à rotation est plus grande que kT , l'orientation est soutenue.

5. ^4He

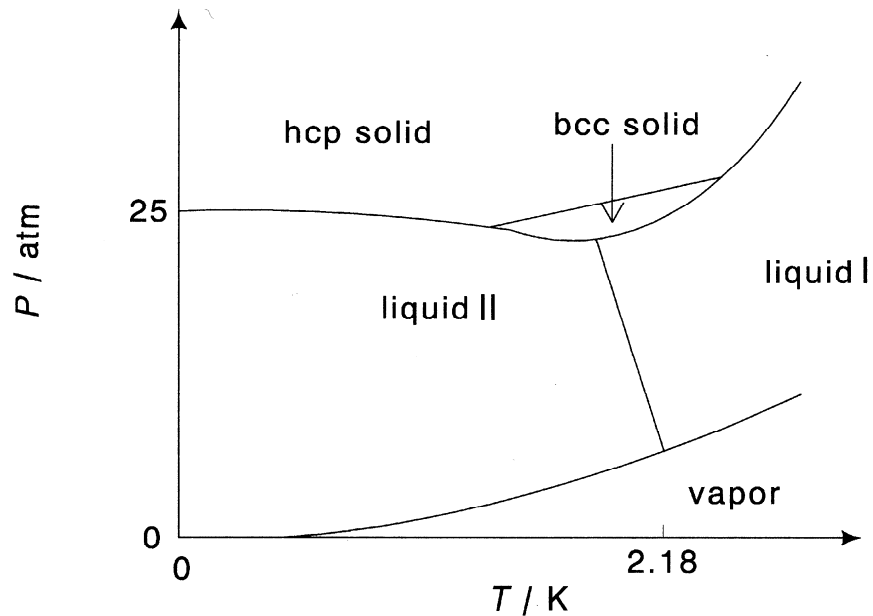


Figure 9.12. Phase diagram of ^4He .

Les 2 phases solides peuvent exister seulement sous hautes pressions

Il y a 2 phases liquides avec des propriétés uniques. Le liquide-I a un point d'ébullition de 4.2 K (fluide extrêmement froid). Le liquide-II a zéro viscosité et une conductivité thermique 1000 fois plus grande que le cuivre au voisinage de la transition I-II.

6. Le carbone

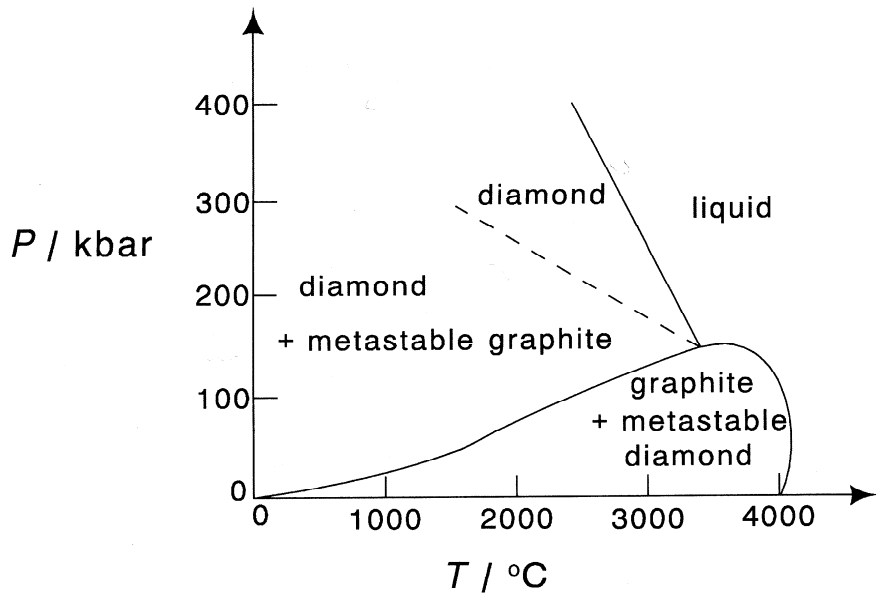
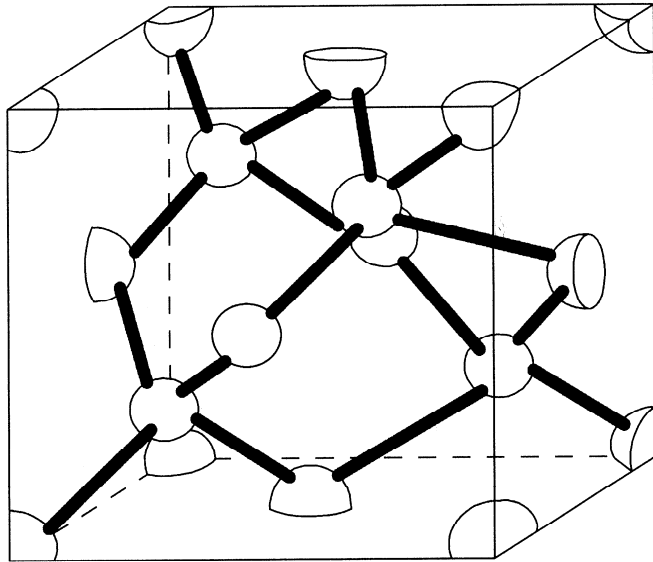


Figure 9.13. The pressure–temperature phase diagram of carbon. Solid lines indicate the regions of stable phases; metastability is indicated with dashed lines.

Le graphite est la forme la plus stable à basses pressions, alors que la forme la plus stable à hautes pressions est le diamant.

Le diamant est métastable à l'ambiante, mais la transformation en graphite est très lente.

a.



b.

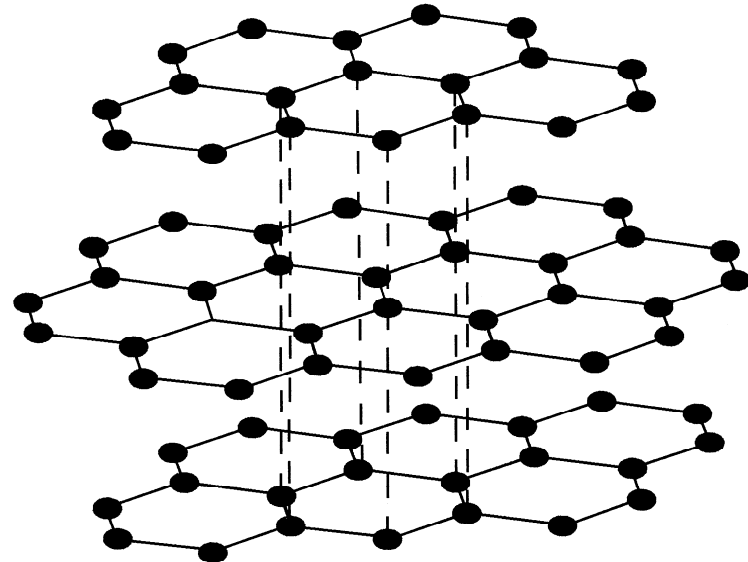
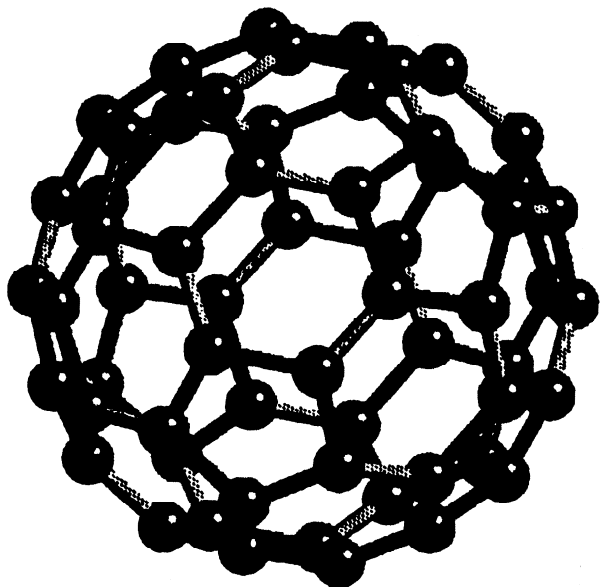


Figure 9.14. Two polymorphs of carbon: (a) diamond and (b) graphite. The three-dimensional bonding network of diamond is one of the reasons why diamond is so hard. On the other hand, the layered structure of graphite, with the layers held together with weak van der Waals interactions, makes graphite useful as a lubricant.

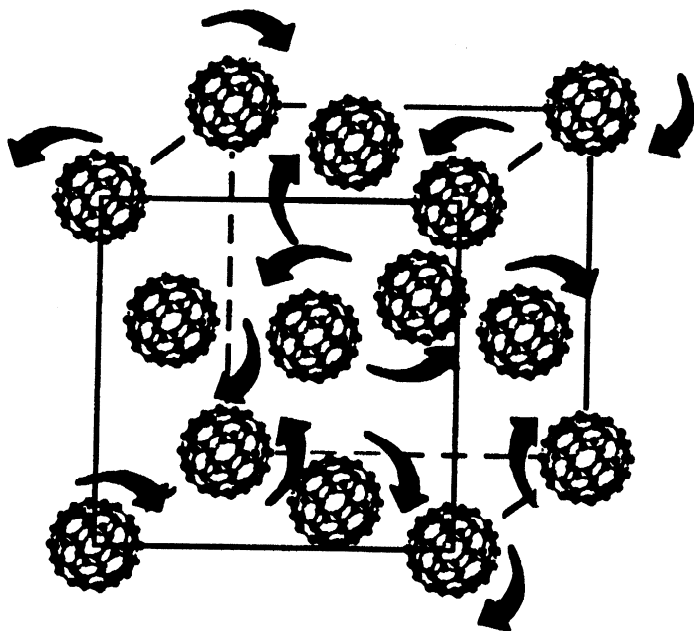
Polymorphisme du carbone: structures de diamant et graphite.

Figure 9.15. The molecular structure of C_{60} .



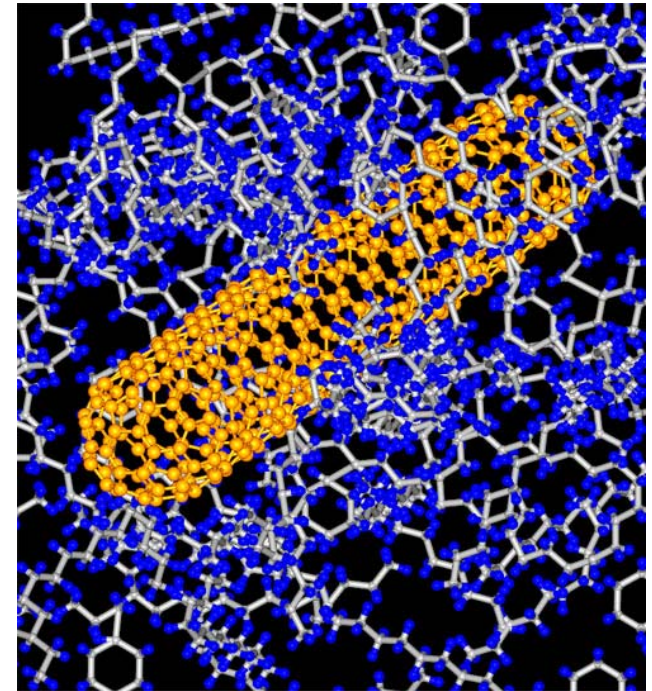
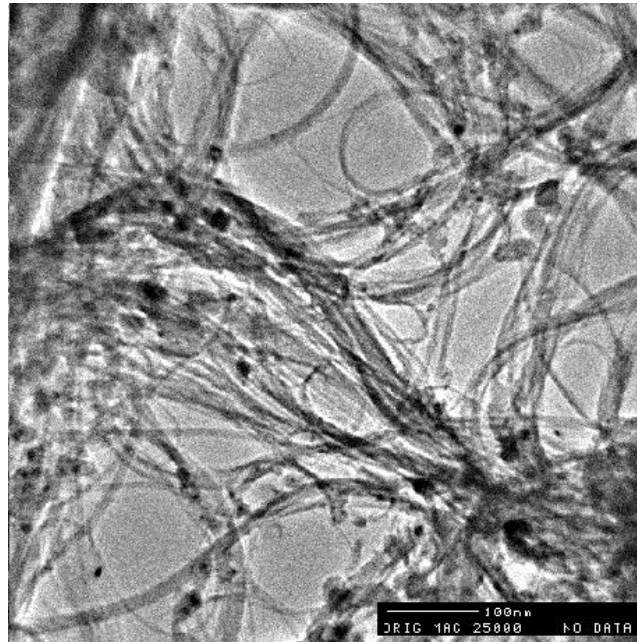
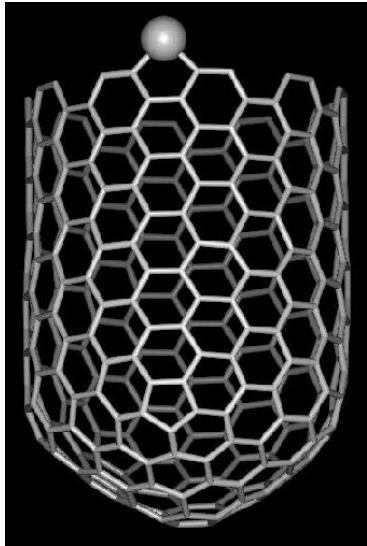
Une 3e forme du carbone: **Fullerènes**
 C_{60} : ballon de soccer, un atome de carbone à chaque sommet, 20 hexagones et 12 pentagones; propriétés optiques et électroniques uniques.

Figure 9.16. The structure of C_{60} at room temperature, showing the C_{60} molecules dynamically orientationally disordered on their face-centered cubic lattice sites.



Nanotubes de carbone: feuilles de graphite roulées, formant des cylindres concentriques.

Beaucoup de potentiels pour la nanotechnologie



Composites polymère/nanotube de carbone

La règle de phase de Gibbs

Établir une relation entre le nombre des variables libres spécifiant l'état d'un système et le nombre des composants chimiques présents ainsi que le nombre des phases présentes dans le système.

Le **degré de liberté F** (nombre des variables indépendantes requis pour spécifier un système contenant **C** composants et **P** phases) est donné par:

F = nombre des variables – nombre des relations décrivant les conditions d'équilibre

= 2 [T, P] + P (C-1) [(C-1) fractions molaires pour chaque phase] - C(P-1) [(p-1) équations pour égalité du potentiel chimique pour chaque composant]

$$F = 2 + C - P$$

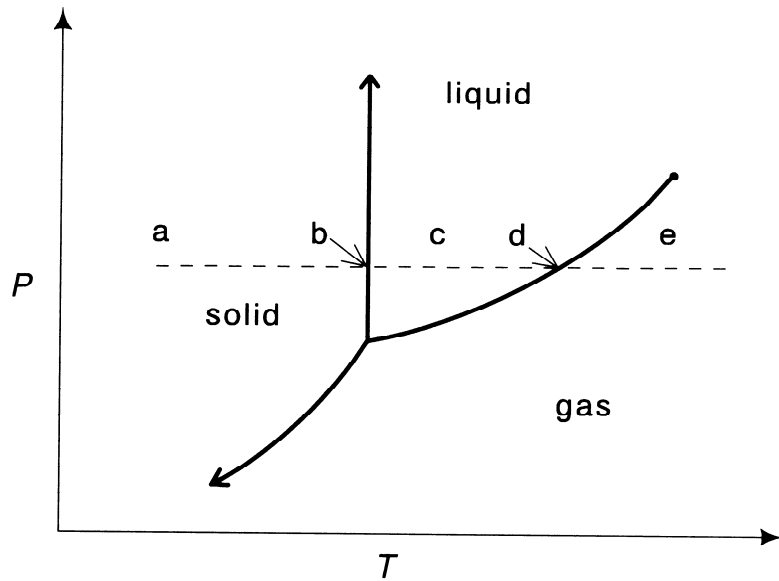


Figure 9.19. Phase diagram for a typical pure material, showing the effect of pressure and temperature on phase stability. The solid lines indicate stable phase boundaries. The dashed line indicates heating at constant pressure (see text).

- $F=2$ à l'intérieur de la région de chaque phase
- $F=1$ sur les frontières (équilibres) entre deux phases
- $F=0$ au point triple

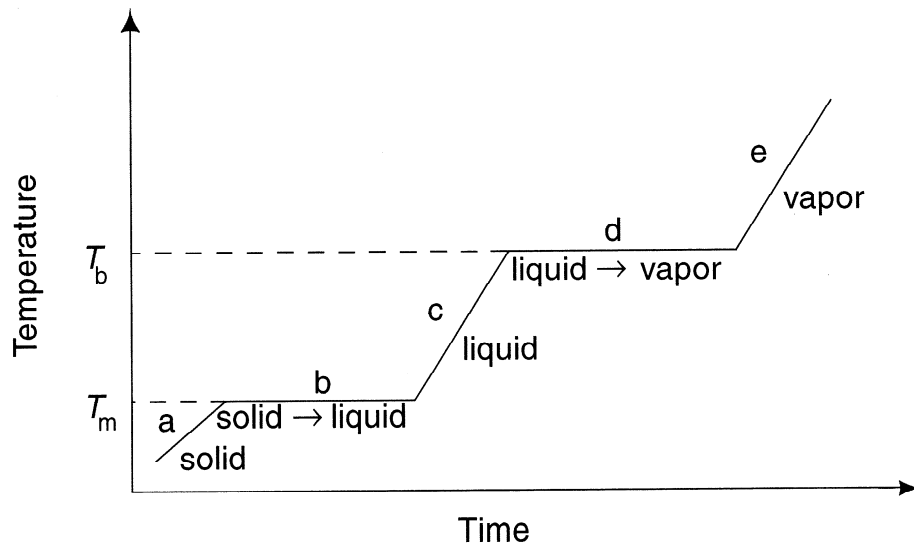


Figure 9.20. The warming curve (temperature–time profile) corresponding to isobaric heating of a pure material from solid to liquid to gas (i.e., along the dashed line of Figure 9.19).

Les plateaux b et d correspondent à $F=0$ (P fixée).
 Utile pour construire un diagramme de phase.

Diagrammes de phase de solutions binaires liquide-liquide

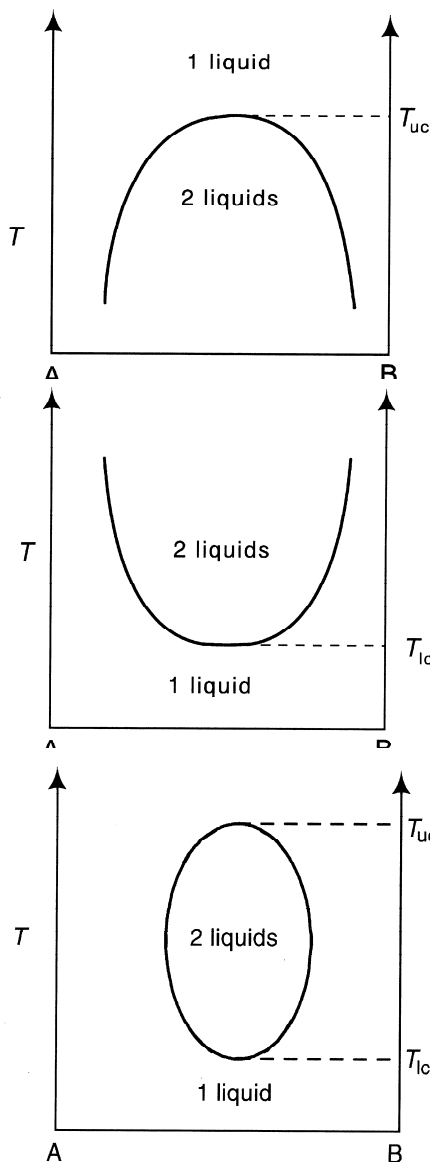


Figure 9.21. An example of a liquid–liquid system with increased solubility at increased temperature, showing an upper consolute temperature, T_{uc} , at a composition intermediate between pure A and pure B. An example of such a phase diagram is water–aniline, with $T_{uc} = 441$ K.

Figure 9.22. An example of a liquid–liquid system with increased solubility at decreased temperature, showing a lower consolute temperature, T_{lc} , at a composition intermediate between pure A and pure B. An example of such a phase diagram is water–triethylamine, with $T_{lc} = 291.6$ K.

Figure 9.23. A liquid–liquid system showing both an upper consolute temperature and a lower consolute temperature, both at compositions intermediate between pure A and pure B. An example of such a phase diagram is water–nicotine, with $T_{uc} = 480$ K and $T_{lc} = 335$ K.

Mélangeant 2 ou plus de composants est un moyen pour ajuster les propriétés existantes ou obtenir de nouvelles propriétés – une approche importante pour la science des matériaux.

Système miscible (une phase liquide) ou immiscible (deux phases liquides) en fonction de la température et de la composition.

Diagrammes de phase de solutions binaires liquide-vapeur

Solutions idéales: la loi de Raoult

$$P_A = X_A P_A^0$$

$$P_{\text{tot}} = X_A P_A^0 + X_B P_B^0$$

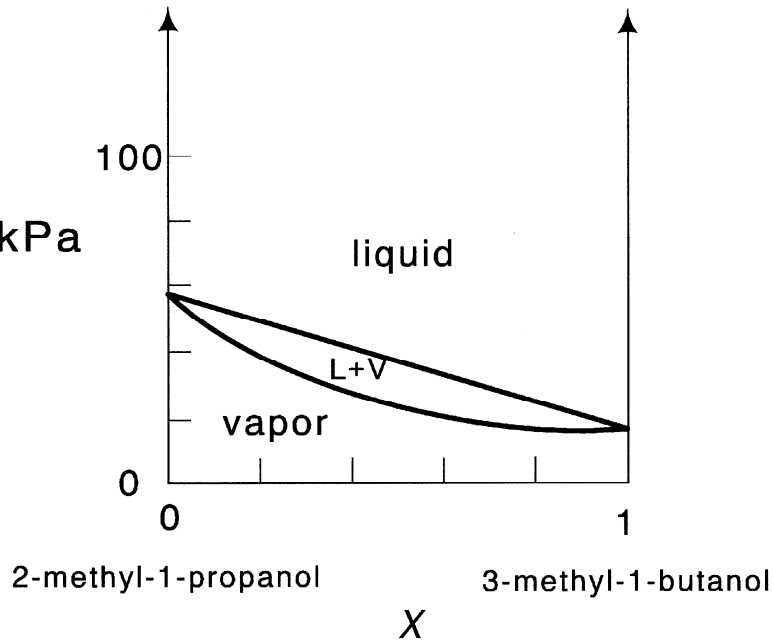


Figure 9.24. The pressure–composition diagram for 2-methyl-1-propanol with 3-methyl-1-butanol, $T = 323.1$ K, which forms a nearly ideal solution. The liquid curve is nearly a straight line, as given by Equation 9.21.

même interaction pour A-A, B-B et A-B

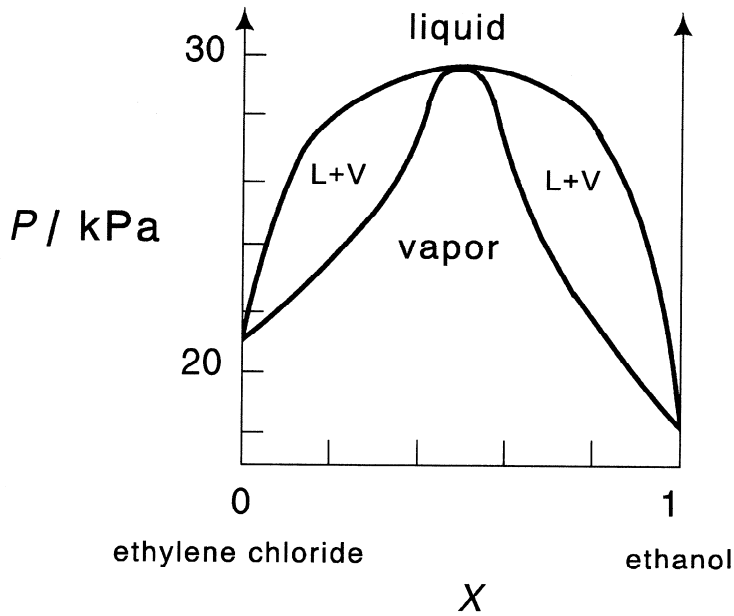


Figure 9.25. The liquid–vapor phase diagram for the system ethylene chloride–ethanol at $T = 313.1$ K, showing pressures greater than ideal pressures, and an azeotrope.

Solutions non-idéales, point azéotrope

interaction A-B moins attractive que A-A et B-B

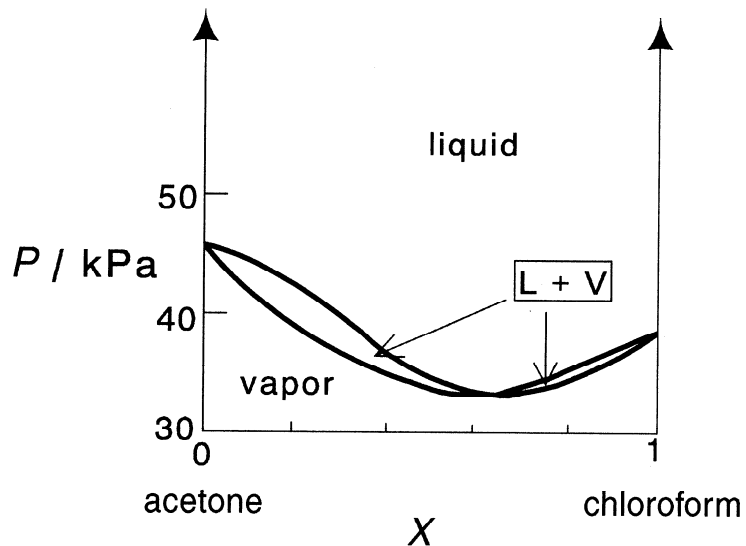


Figure 9.26. A liquid–vapor diagram showing a low vapor pressure azeotrope. The components are acetone and chloroform at $T = 308$ K.

interaction A-B plus attractive que A-A et B-B

Même analyse pour les diagrammes de phase Température-Composition (distillation), et l'utilisation de la règle de levier pour déterminer les proportions de la phase liquide et la phase vapeur.

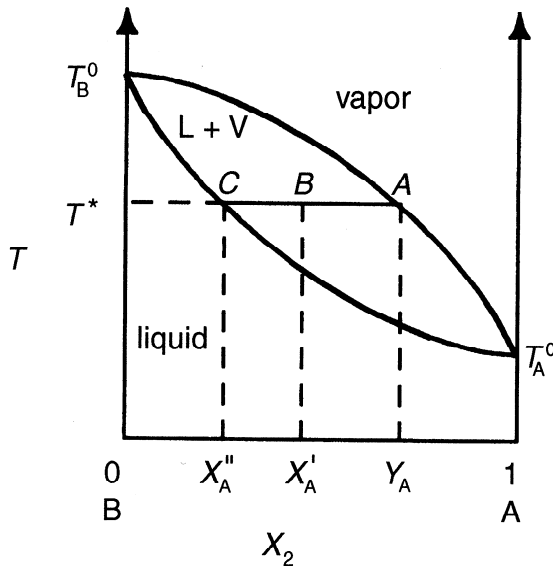


Figure 9.30. A boiling point diagram for an ideal solution, for purposes of illustrating the lever principle.

$$\frac{n_{\text{liq}}}{n_{\text{vap}}} = \frac{Y_A - X_A'}{X_A' - X_A''} = \frac{AB}{BC}$$

Diagrammes de phase de solutions binaires liquide-solide

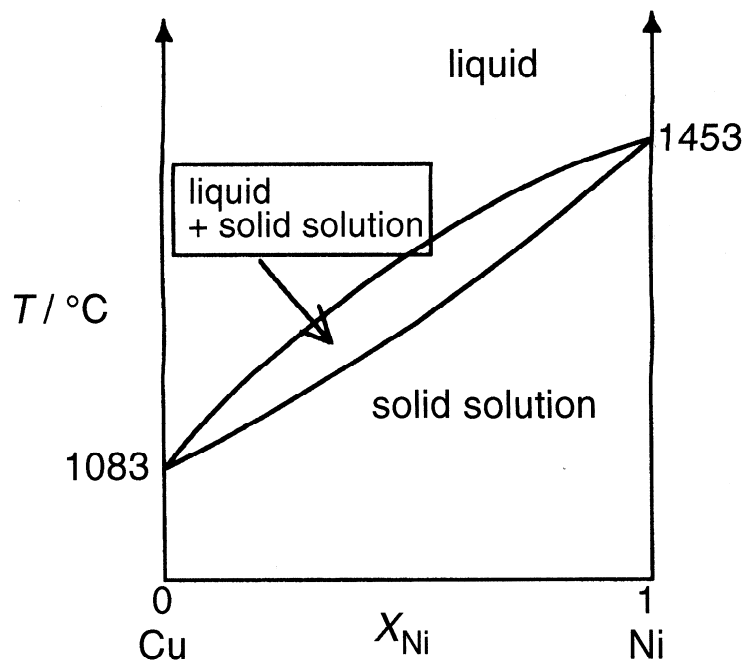


Figure 9.31. Melting point diagram for copper with nickel. Note that only at the pure metal compositions is the melting point at one fixed temperature; at all other compositions, there is a temperature range over which liquid and solid coexist.

Solution solide: mélange miscible, favorisée par les rayons atomiques similaires et une même maille cristalline.

Généralement, deux solides ne sont pas miscibles à cause de l'incompatibilité de leurs structures cristallines. Dans ce cas, une suspension ou dispersion d'un solide dans l'autre est souvent formée.

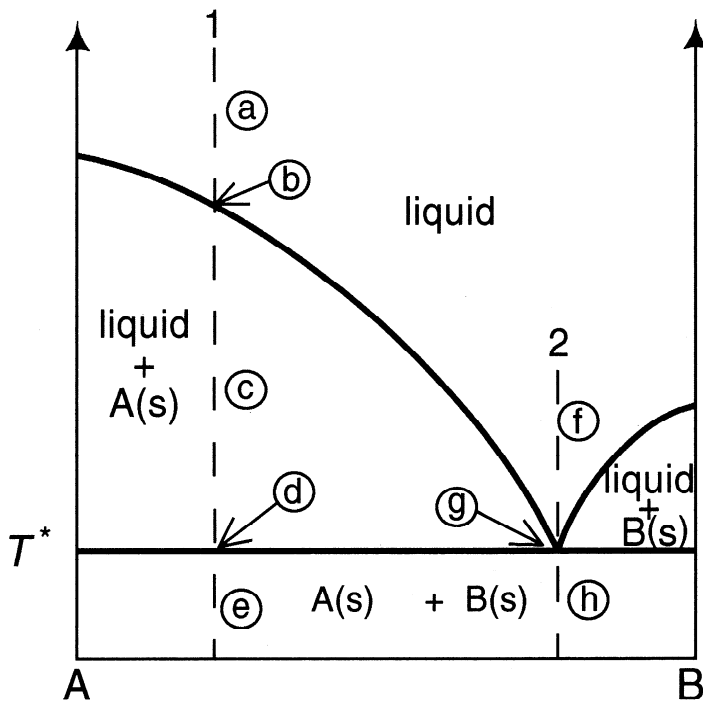


Figure 9.33. A freezing point diagram showing completely immiscible solid phases. The constant-composition slices shown correspond to the cooling curves shown in Figures 9.34 and 9.35.

Analyse de la courbe de refroidissement avec la règle de phase le long de la tranche 1 et de la tranche 2.

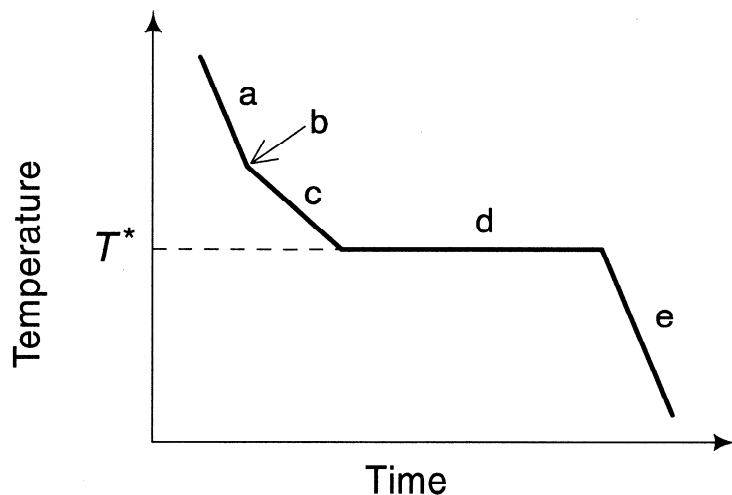


Figure 9.34. The cooling curve (temperature as a function of time) along Slice 1 of the phase diagram shown in Figure 9.33. Note the break at b and halt at d.

La tranche 1

TABLE 9.1.

The Phases and Degrees of Freedom in the Various Regions of the Phase Diagram along Slice 1, shown in Figure 9.33.^a

Region	Phase(s)	p	F
a	Liquid	1	2
b	Liquid + A(s)	2	1 (break)
c	Liquid + A(s)	2	1
d	Liquid + A(s) + B(s)	3	0 (halt)
e	A(s) + B(s)	2	1

^a $P = 1 \text{ atm}$; $F = 3 - p$.

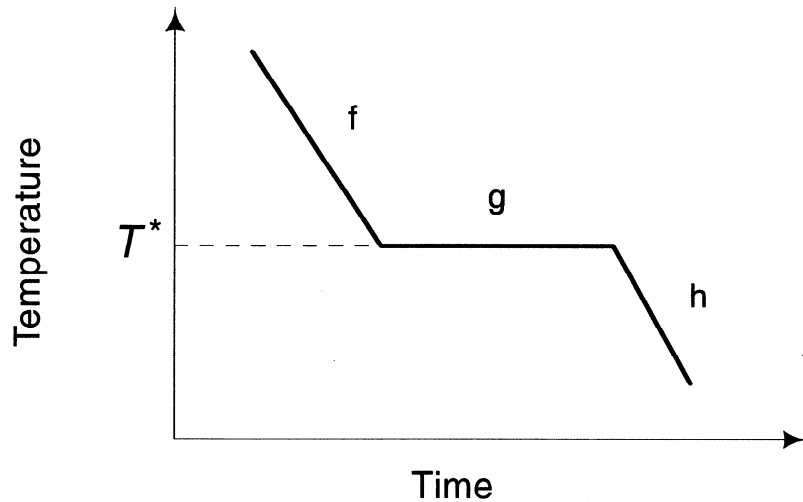


Figure 9.35. The cooling curve (temperature as a function of time) along Slice 2 of the phase diagram in Figure 9.33 at a constant pressure of 1 atm. Note the halt at g.

La tranche 2

TABLE 9.2.

The Phases and Degrees of Freedom in the Various Regions of the Phase Diagram along Slice 2, shown in Figure 9.33.^a

Region	Phase(s)	p	F
f	Liquid	1	2
g	Liquid + A(s) + B(s)	3	0 (halt)
h	A(s) + B(s)	2	1

^a $P = 1 \text{ atm}$; $F = 3 - p$.

Le point g correspond à la composition eutectique, à laquelle les solides fondent à la même température.

Diagrammes de phase des systèmes ternaires (3 composants)

Généralement, un diagramme de phase à 2-dimension est construit avec:

1. T – P pour un matériau pur (un composant).
2. T – composition (P constante) ou P – composition (T constante) pour un système binaire (2 composants).
3. Composition-composition (T et P constantes) pour un système ternaire

9.11 Three-Component (Ternary) Phase Diagrams 191

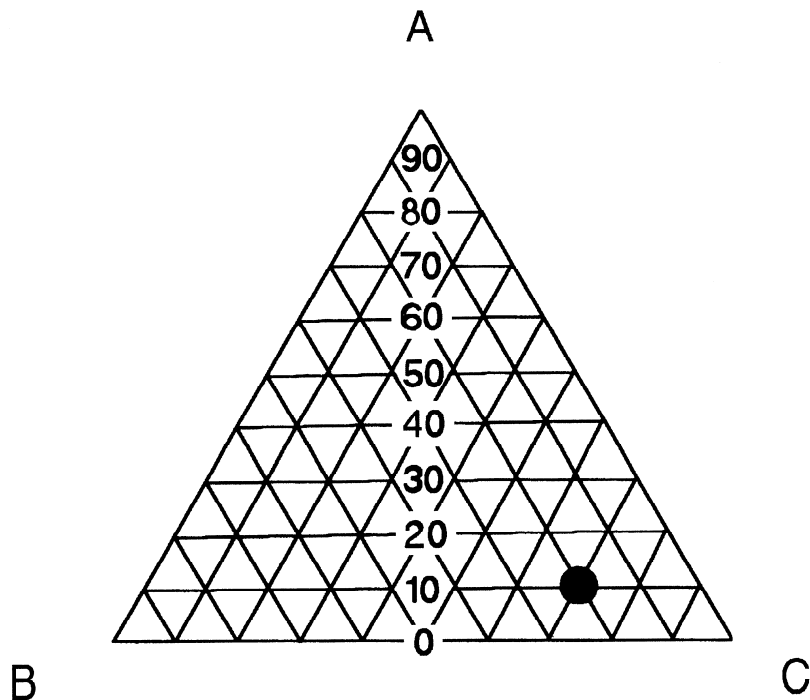


Figure 9.44. Triangular coordinates to represent the constant-temperature, constant-pressure phase diagram of the A–B–C ternary system. Each vertex represents the pure component (A, B, or C, as labeled), and each side presents a binary phase diagram (A–B, opposite vertex C; A–C, opposite vertex B; B–C, opposite vertex A). The interior of the triangle represents nonzero compositions of all three components. The numbers shown correspond to A concentration. The point marked ● represents 10% A, 20% B, 70% C.

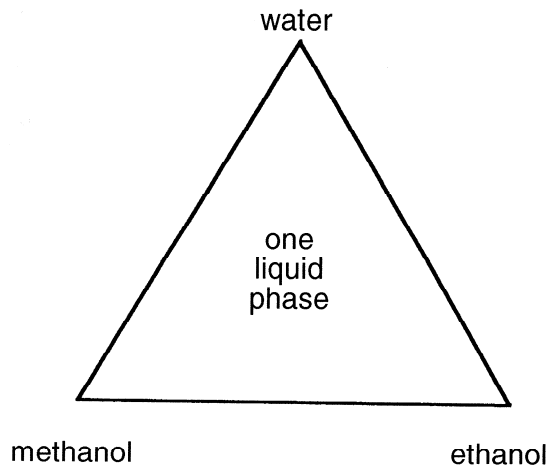


Figure 9.45. Ethanol–methanol–water phase diagram at $T = 25^\circ\text{C}$, $P = 1\text{ atm}$. All three liquid components are miscible in all proportions.

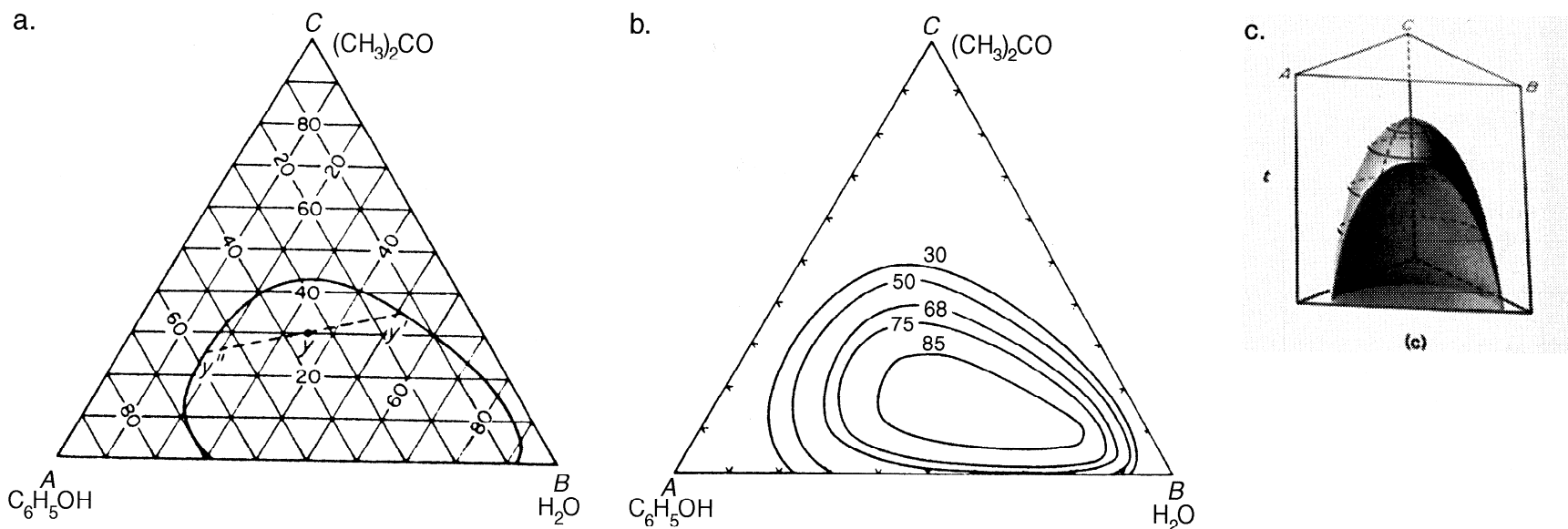


Figure 9.46. The ternary system, phenol–water–acetone: (a) at room temperature; (b) as a function of temperature; (c) showing temperature as an additional dimension (vertical axis), clearly indicating the upper consolute temperature (temperature above which the system gives rise to only one liquid phase, regardless of the proportions). Reproduced, with permission, from W.J. Moore (1962) *Physical Chemistry*, 3rd Edition, Prentice-Hall.

Chapitre 10

Phénomènes interfaciales et de surface

Les surfaces des matériaux peuvent avoir des propriétés qui se distinguent des propriétés de masse (bulk).

Les propriétés de surface manifestent de façon importante pour les matériaux ayant une grande surface spécifique ($\text{cm}^2 \text{g}^{-1}$).

Une propriété importante de surface est la capacité d'interagir avec d'autres atomes ou molécules absorbés dans l'intérieur (**absorption**) ou adsorbés sur la surface (**adsorption**).

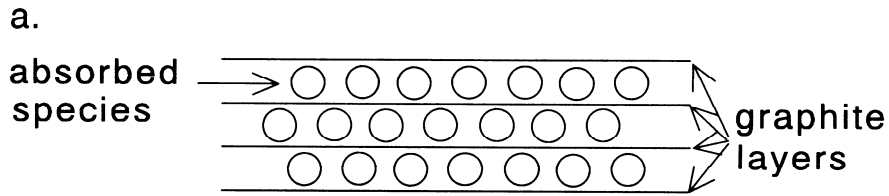
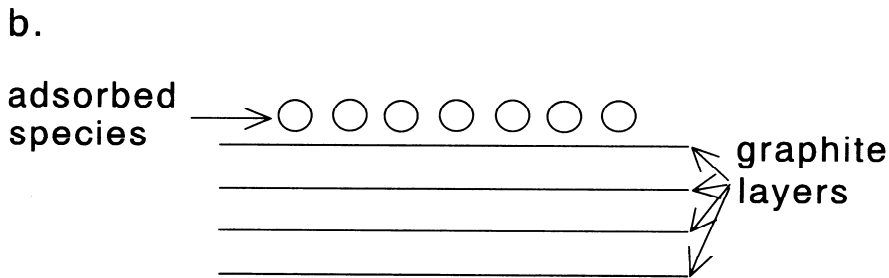


Figure 10.1. Cross-sectional views of absorption into and adsorption onto graphite. (a) Atoms or molecules can be absorbed into a graphite structure to form a graphite intercalate. (b) Atoms or molecules also could be adsorbed onto a graphite structure.



Si l'adsorption d'une espèce (l'adsorbat) sur la surface d'un substrat (l'adsorbant) n'implique pas la formation de liaisons chimiques, c'est une **physisorption**, avec une énergie interactionnelle relativement faible ($\Delta H \sim -20 \text{ KJ mol}^{-1}$).

Dans le cas contraire, c'est une **chimisorption**, avec une énergie interactionnelle plus forte ($\Delta H \sim -200 \text{ KJ mol}^{-1}$).

Énergie de surface: tension de surface

L'énergie libre de Gibbs de surface est toujours plus grande que celle en volume. Les atomes ou molécules en surface ne peuvent pas avoir les liaisons ou interactions dans toutes les directions, alors que ceux à l'intérieur peuvent.

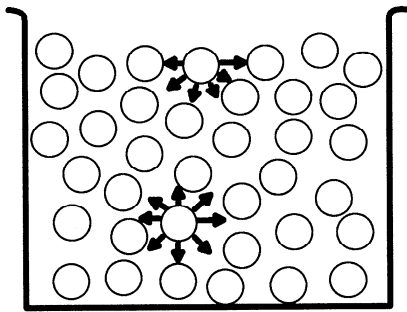


Figure 10.6. The attractive interaction of molecules with each other in liquids leads to no net force on an interior molecule, but a net inward force on surface molecules.

La tension de surface (γ) est l'énergie requise pour augmenter une unité de surface (J m^{-2}):

$$\gamma = dG/dA$$

G: énergie libre de Gibbs; A: surface

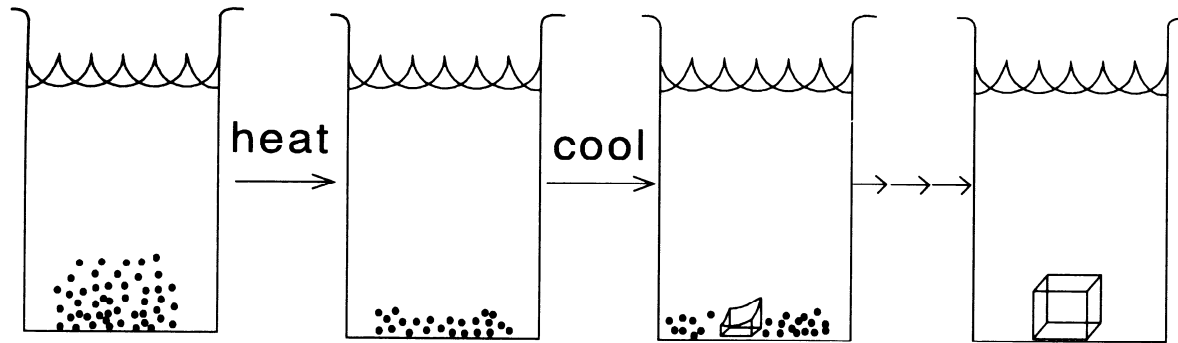


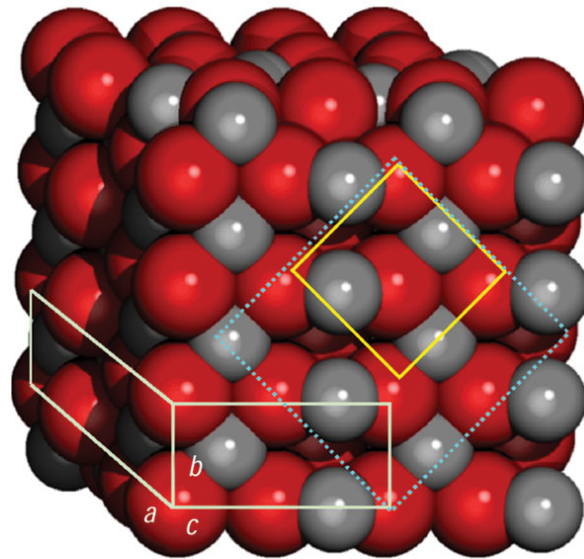
Figure 10.2. This diagram shows schematically how a group of small crystals (e.g., a powder) can be transformed to one large crystal, if the material is more soluble when the solution is heated (as is usual). Heat leads to greater solubility and cooling causes preferential precipitation on a seed crystal. After a number of cycles, powder can be transformed into a single crystal. This process is thermodynamically favored on the basis of lowered Gibbs energy for the sample with the lowest surface area (one large crystal).

TABLE 10.1.
Surface Energies, G_s , of Some Materials.^a

Material	$G_s / \text{J m}^{-2}$
Metal	~ 1
Metal oxide	~ 0.3
Ice	~ 0.1
Wax	~ 0.07

^a Data from R.G. Linford (1972), *Chemical Society Review*, **1**, 445.

Selon une prédiction théorique et des évidences expérimentales, des céramiques nanocristallines et poreuses (oxydes d'aluminium) peuvent avoir une **énergie de surface négative** pour certaines facettes de cristaux en raison des molécules H₂O adsorbées et dissociées, ce qui fait que ces nanomatériaux poreux sont très stables même à hautes températures.



Structure atomique de Θ -Al₂O₃ (sphères rouges: oxygène; sphères grises: aluminium).
Nature Materials 2004, 5, 289.

Étude de surfaces

Le microscope à effet tunnel (STM: scanning tunneling microscope) possède une résolution atomique.

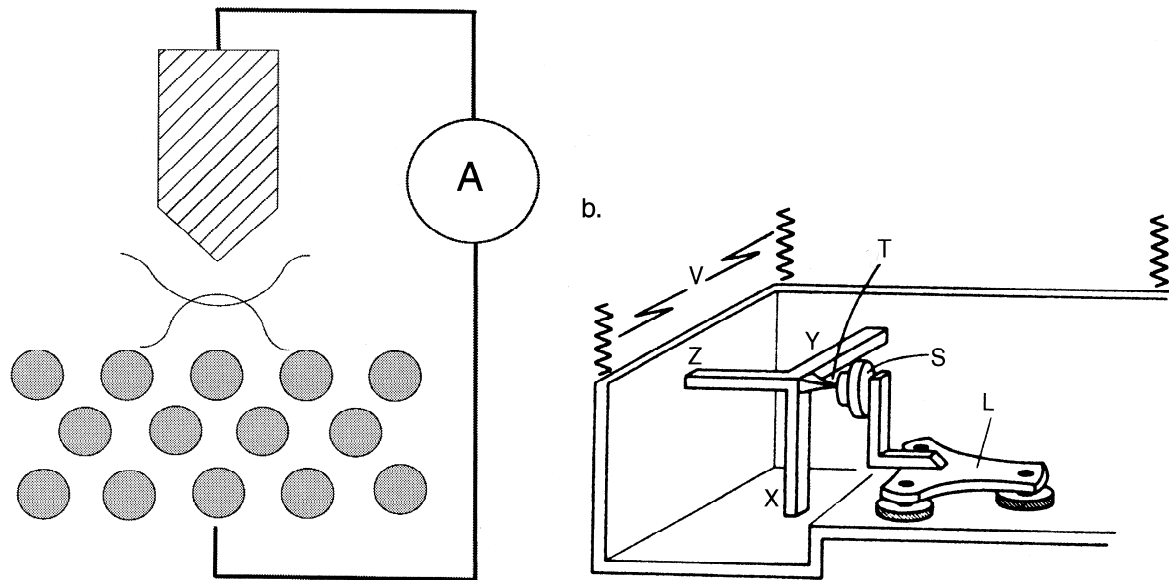


Figure 10.3. (a) A schematic view of the scanning tunneling microscope. The overlap of the wavefunctions of the surface atoms with the scanning tip (“wand”) completes the circuit and allows a measurable tunneling current. (b) The first scanning tunneling microscope, showing a piezotripod (X–Y–Z) for fine positioning of the tip T and a piezomotor L for rough positioning of the sample S. Reprinted, with permission, from Ch. Gerber, G. Binnig, H. Fuchs, O. Marti, and H. Rohrer (1986), *Review of Scientific Instruments*, **57**, 221, copyright American Institute of Physics.

Lorsque le chevauchement des fonctions d’onde de la pointe conductrice et des atomes à la surface est suffisamment important, des électrons libres ‘sautent’ par effet tunnel, ce qui résulte d’un courant électrique.

Mesure de la tension de surface et la capillarité

1) Pour une goutte sphérique de rayon R , une contraction de dR , ce qui diminue G , est contrebalancée par le travail effectué contre la différence des pressions à l'intérieur et à l'extérieur de la goutte.

$$\Delta P 4\pi R^2 dR = 8\pi R \gamma dR$$

$$\Delta P = \frac{2\gamma}{R} .$$

et pour une bulle de savon?

TABLE 10.2.
Surface Tension, γ , for Some Liquids at $T = 25^\circ\text{C}^a$

Liquid	$\gamma / 10^{-3} \text{ J m}^{-2}$
Br_2	40.95
H_2O	71.99
Hg	485.48
CS_2	31.58
CH_3OH	22.07
CH_3NH_2	19.15
$\text{CH}_3\text{CH}_2\text{OH}$	21.97

^a Data from J.J. Jasper (1972), *Journal of Physical and Chemical Reference Data*, **1**, 841.

2) La masse d'une goutte en chute libre est liée à la tension de surface.

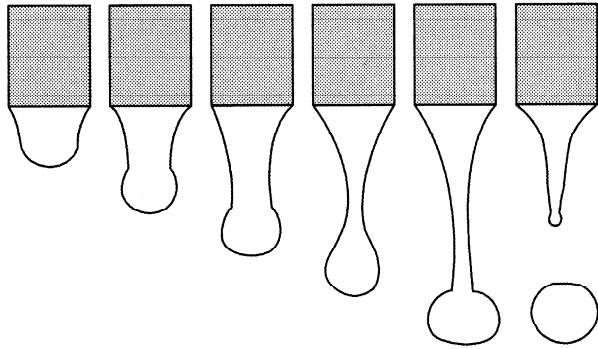


Figure 10.8. The sequence of shapes for a drop falling from an open tube. Note the residual liquid after the drop is detached.

$$m_{\text{ideal}} = 2\pi r\gamma/g$$

$$m_{\text{obs}} = fm_{\text{ideal}}$$

TABLE 10.3.
Correction Factors for the Drop Weight
Method of Determining Surface Tension^a

$r/V^{1/3}$	f
0.30	0.7256
0.40	0.6828
0.50	0.6515
0.60	0.6250
0.70	0.6093
0.80	0.6000
0.90	0.5998
1.00	0.6098
1.10	0.6280
1.20	0.6535

^a r is the tube radius and V is the volume of the drop.

3) Ascension capillaire

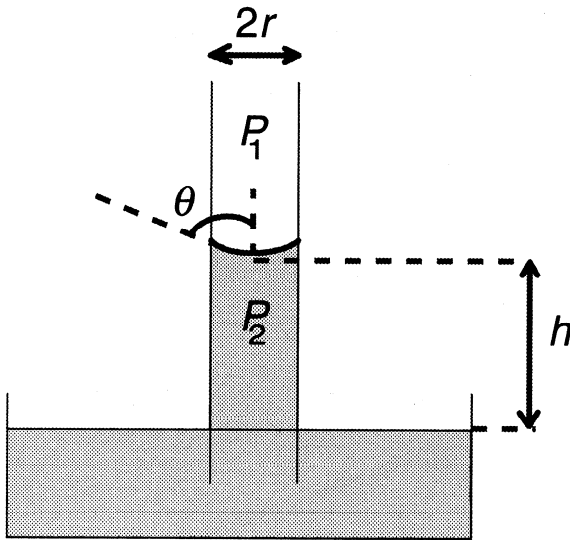


Figure 10.9. Rise of water in a glass capillary.

Un liquide (H_2O) va mouiller le verre si sa tension de surface est plus petite que celle du verre. Une montée du liquide dans le tube capillaire va se produire pour générer une pression hydrostatique et ainsi balancer les pressions.

$$\Delta P = \frac{2\gamma}{R} = \frac{2\gamma \cos \theta}{r}$$

$$\rho g h = \frac{2\gamma \cos \theta}{r}$$

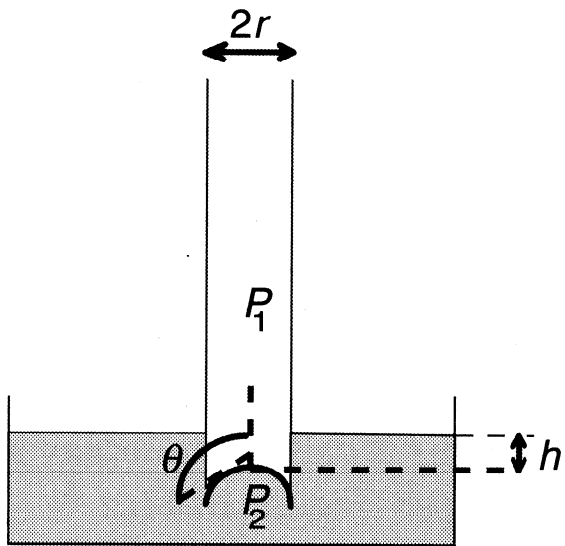


Figure 10.10. Mercury is depressed in a glass capillary.

Dans le cas contraire (Hg, par exemple),
une dépression capillaire se produira.

Films liquides de surface

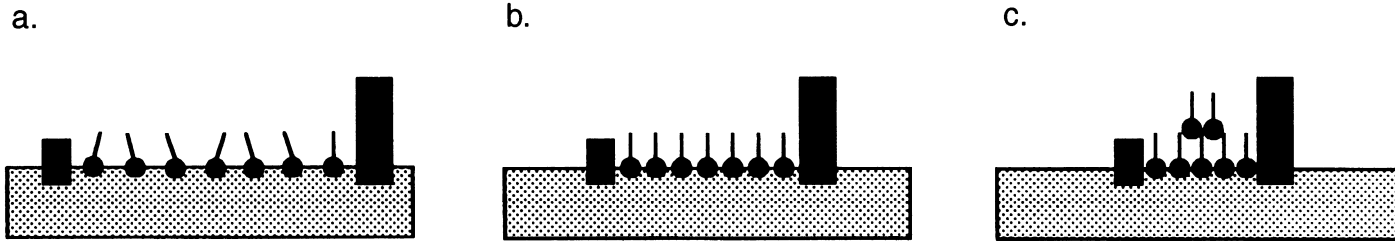


Figure 10.11. (a) A schematic view of surfactant molecules at low surface coverage on water. The polar head groups point into the water and the nonpolar tails point out of the water. (b) As the pressure is increased (i.e., the surface area is decreased), a one-molecule-thick film (monolayer) is formed. (c) At higher pressures, the film collapses. Here the pressure is defined as the force per unit length of the edge of the monolayer. The nonpolar tails of the surfactant molecules would be dynamically disordered.

Molécules amphiphiles dans l'eau

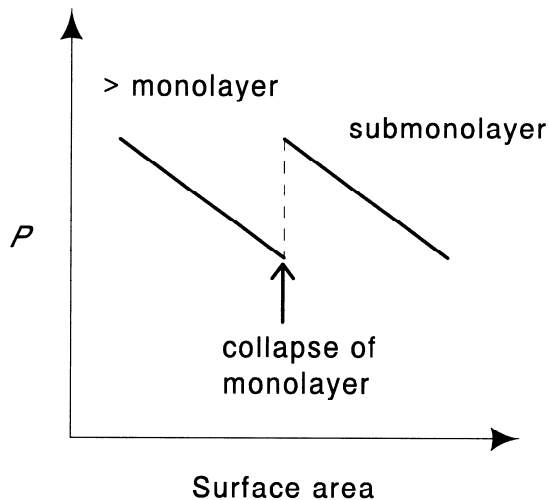


Figure 10.13. Two-dimensional pressure vs. area relationship for a Langmuir-Blodgett film showing the collapse of the film as the surface area is decreased.

Films Langmuir-Blodgett: arrangement régulier des molécules

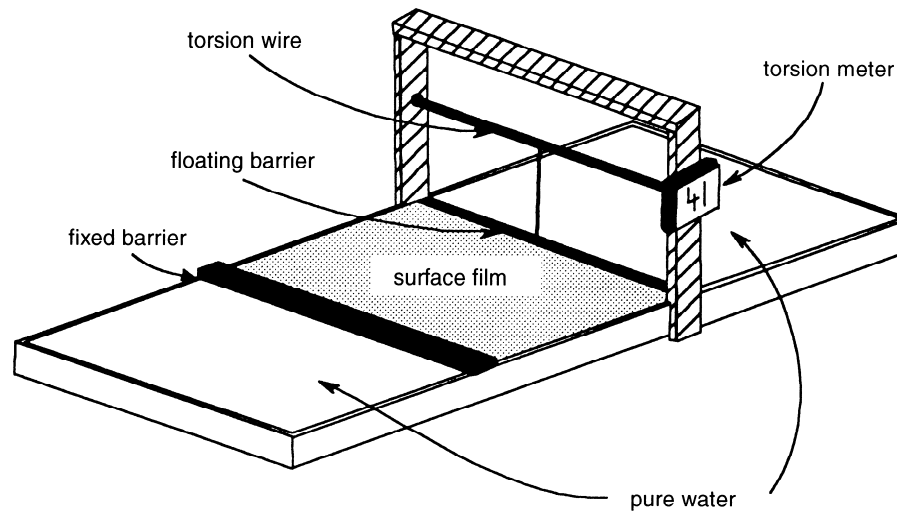


Figure 10.12. A schematic diagram of a floating-barrier trough for measuring the pressure of surface films. This is commonly referred to as a Langmuir trough.

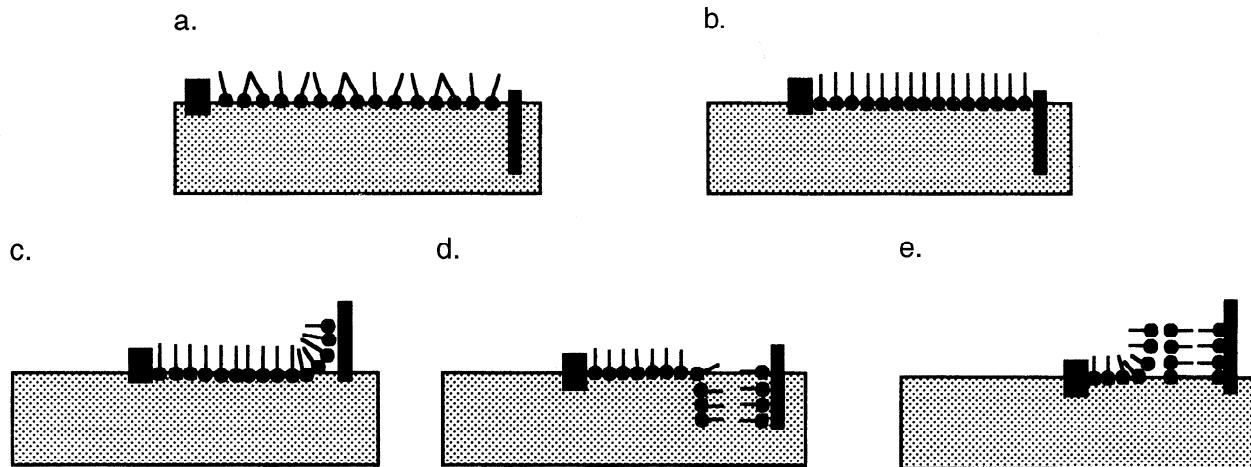


Figure 10.14. (a–e) Deposition of a Langmuir-Blodgett film on a solid substrate by successive passes of a movable barrier. In this case the layers are all head-to-head and tail-to-tail.

Monocouche ou multicouche peut être déposée sur la surface d'un substrat solide, pouvant produire des matériaux intéressants.

Surface de commande

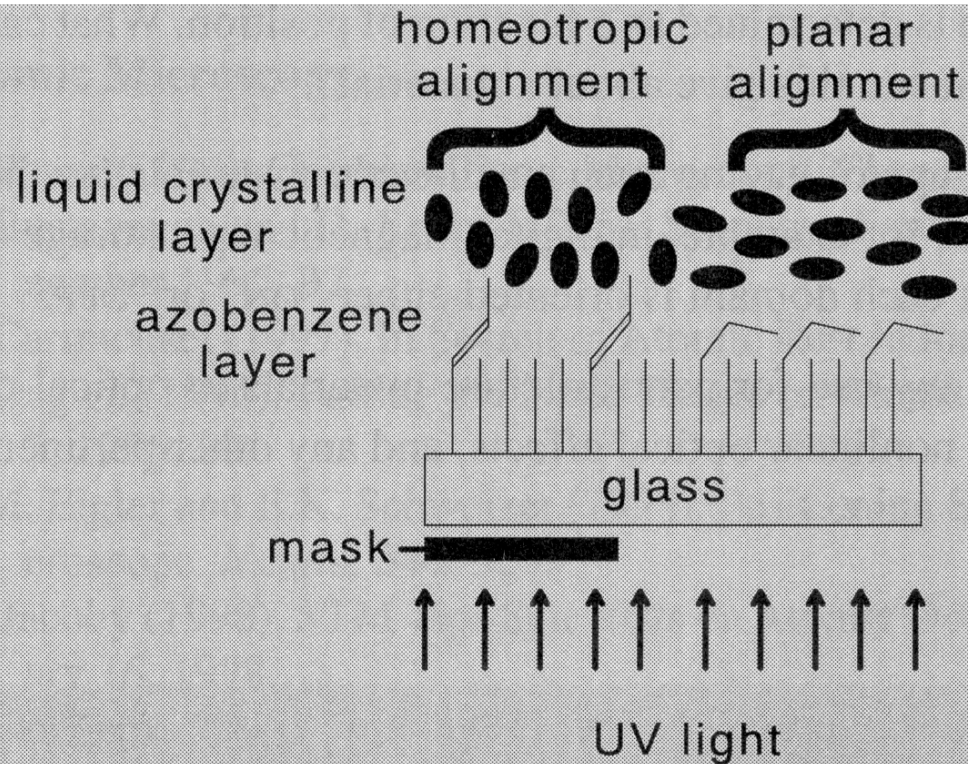


Figure 10.15 Light induces a change in the orientation of the azobenzene layer in this coating which, in turn, changes the orientation of the liquid crystalline layer and the optical and electrical properties of this assembly in the area in which the light is not masked.