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Microscopic Origin of Thermodynamics

Problem 1.1 Using the phase rule, justify whether the following thermodynamic systems are adequately defined:

(i) a pure liquid of known mass at given temperature and density;
(ii) a pure liquid of known mass at given density and pressure;
(iii) a two-phase system at given temperature, pressure, and the mole fractions of all chemical species in one phase;
(iv) an ionic liquid containing two types of cations and one type of anions at given temperature, pressure, and the ionic composition.

Solution

The phase rule indicates that, for a bulk system with C chemical species and P phases without chemical reaction, $N_f = C - P + 2$ intensive variables are needed to define a thermodynamic state. In addition, one extensive variable is required to define the system size.

(i) Yes, here $C = 1$ and $P = 1$, thus $N_f = 2$. Temperature and density are independent intensive variables, mass is an extensive quantity.
(ii) The specification could be problematic because pressure and density are conjugated variables. For example, liquid water exhibits a maximum density at 1 atm and 4 °C, implying that there could be two temperatures for one density at the same pressure.
(iii) No, the system is over specified. $P = 2$ then $N_f = C$. But temperature, pressure, and the compositions of one phase constitute $C + 1$ independent intensive variables.
(iv) Here $C = 2$ (two ion pairs), $P = 1$ and $N_f = 3$. The intensive variables are well defined but the system size is unknown.

Problem 1.2 Based on the fundamental thermodynamic relations, show

$$\left(\frac{\partial C_P}{\partial P}\right)_{T,N} = -T\left(\frac{\partial^2 V}{\partial T^2}\right)_{P,N}.$$

Solution

First, write the constant-pressure heat capacity in terms of entropy

$$C_P = T\left(\frac{\partial S}{\partial T}\right)_{P,N}.$$

Taking a partial derivative with respect to P at constant T and N leads to

$$\left(\frac{\partial C_P}{\partial P}\right)_{T,N} = T\left(\frac{\partial^2 S}{\partial T \partial P}\right)_{N}.$$

Solutions Manual to Fundamentals and Practice in Statistical Thermodynamics,
First Edition. Jianzhong Wu and John M. Prausnitz.

From the Maxwell relation

$$\left(\frac{\partial S}{\partial P}\right)_{T,N} = -\left(\frac{\partial V}{\partial T}\right)_{P,N},$$

we then have

$$\left(\frac{\partial^2 S}{\partial T \partial P}\right)_N = -\left(\frac{\partial^2 V}{\partial T^2}\right)_{P,N} \Rightarrow \left(\frac{\partial C_P}{\partial P}\right)_{T,N} = -T\left(\frac{\partial^2 V}{\partial T^2}\right)_{P,N}.$$

Problem 1.3 Acoustic velocity, or the speed of sound, in a fluid can be derived from the first law of thermodynamics for steady-state flow processes

$$d(\hat{H} + v_s^2/2) = 0$$

in combination with the mass-balance equation

$$d(\hat{\rho} v_s) = 0.$$

Here, $\hat{H}$ is the specific enthalpy of the fluid, $\hat{\rho}$ is the mass density, and v_s is the velocity of the elastic wave, i.e., the sound speed.

(i) Derive the following expression from the 1st law and mass balance

$$v_s = \sqrt{\left(\frac{\partial P}{\partial \hat{\rho}}\right)_S}.$$

(ii) Show that the partial derivative at constant entropy S can be expressed in terms of measurable quantities

$$v_s = \sqrt{\frac{\gamma}{\hat{\rho}\kappa_T}},$$

where $\gamma \equiv C_P/C_V$ is the ratio of the constant-pressure and constant-volume heat capacities of the fluid, κ_T is the isothermal compressibility

$$\kappa_T \equiv -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T.$$

(iii) Predict the speed of sound in the atmosphere at 25 °C. Assuming atmosphere is an ideal gas with molar heat capacity $C_P = 29.3\,\mathrm{J/(mol\,K)}$ and molecular weight $M = 29\,\mathrm{g/mol}$.

Solution

(i) Combing the 1st law $d\hat{H} = -v_s dv_s$ with the fundamental equation $d\hat{H} = Td\hat{S} + \hat{V}dP$ leads to, at constant entropy,

$$d\hat{H} = \frac{1}{\hat{\rho}}dP = -v_s dv_s,$$

where $\hat{\rho} = 1/\hat{V}$. The expression for the sound speed is obtained by dividing the above equation by that from the mass balance, $v_s d\hat{\rho} = -\hat{\rho} dv_s$,

$$v_s = \sqrt{\left(\frac{\partial P}{\partial \hat{\rho}}\right)_S}.$$

(ii) First, we rewrite the partial derivative at constant entropy S in terms the molar volume V:

$$\left(\frac{\partial P}{\partial \hat{\rho}}\right)_S = -\hat{V}^2\left(\frac{\partial P}{\partial \hat{V}}\right)_S = -\frac{V}{\hat{\rho}}\left(\frac{\partial P}{\partial V}\right)_S.$$

To make a connection with measurable quantities, we use the following identities:

$$\left(\frac{\partial P}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V \left(\frac{\partial S}{\partial V}\right)_P \quad \text{(chain rule)}$$

and

$$\left(\frac{\partial P}{\partial S}\right)_V \left(\frac{\partial S}{\partial T}\right)_V = \left(\frac{\partial P}{\partial T}\right)_V; \quad \left(\frac{\partial S}{\partial V}\right)_P \left(\frac{\partial T}{\partial S}\right)_P = \left(\frac{\partial T}{\partial V}\right)_P.$$

Combining these equations leads to

$$\left(\frac{\partial P}{\partial V}\right)_S = -\frac{C_P}{C_V}\left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial T}{\partial V}\right)_P = \frac{C_P}{C_V}\left(\frac{\partial P}{\partial V}\right)_T,$$

where we have used the following equations

$$\frac{C_P}{T} = \left(\frac{\partial S}{\partial T}\right)_P, \quad \frac{C_V}{T} = \left(\frac{\partial S}{\partial T}\right)_V, \quad \left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial T}{\partial V}\right)_P = -\left(\frac{\partial P}{\partial V}\right)_T.$$

Therefore, the partial derivative at constant entropy S becomes

$$\left(\frac{\partial P}{\partial \hat{\rho}}\right)_S = -\frac{V}{\hat{\rho}}\frac{C_P}{C_V}\left(\frac{\partial P}{\partial V}\right)_T = \frac{\gamma}{\hat{\rho}\kappa_T}$$

and

$$v_s = \sqrt{\frac{\gamma}{\hat{\rho}\kappa_T}},$$

where $\gamma \equiv C_P/C_V$ is the ratio of the constant-pressure and constant-volume heat capacities of the fluid, and κ_T is the isothermal compressibility

$$\kappa_T \equiv -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T.$$

(iii) For an ideal gas, the compressibility is

$$\kappa_T^{\mathrm{IG}} = \frac{1}{V}\frac{NRT}{P^2} = \frac{1}{P}$$

and

$$\gamma = \frac{C_P}{C_V} = \frac{C_P}{C_P - R},$$

where R is the gas constant. At 1 atm and 25 °C, the mass density of atmosphere is

$$\hat{\rho} = \frac{MP}{RT} = 1185.4\,\mathrm{g/m^3},$$

where we have used the average molecular weight of air $M = 29\,\mathrm{g/mol}$. Substituting $\hat{\rho} = 1185.4\,\mathrm{g/m^3}$ along with the molar heat capacity $C_P = 29.3\,\mathrm{J/(mol\,K)}$ into the equation for the sound speed yields $v_s \approx 330\,\mathrm{m/s}$.

Problem 1.4 Consider a one-dimensional model for a thermodynamic system containing N identical particles. Assume that the internal energy is completely determined by temperature T, system total length L, and particle number N. Show that the fundamental equation of thermodynamics can be written as

$$dU = TdS + fdL + \mu dN,$$

where temperature, line tension (i.e., negative of the one-dimensional pressure), and chemical pressure are defined as, respectively,

$$T = \left(\frac{\partial U}{\partial S}\right)_{L,N},$$

$$f = \left(\frac{\partial U}{\partial L}\right)_{S,N},$$
$$\mu = \left(\frac{\partial U}{\partial N}\right)_{L,S}.$$

What are the analogs of the Maxwell relations for this one-dimensional system?

Solution

We may derive the fundamental equation of thermodynamics from $U = U(S, L, N)$, which is a linear homogeneous function

$$\begin{aligned} dU &= \left(\frac{\partial U}{\partial S}\right)_{L,N} dS + \left(\frac{\partial U}{\partial L}\right)_{S,N} dL + \left(\frac{\partial U}{\partial N}\right)_{L,S} dN \\ &= TdS + fdL + \mu dN. \end{aligned}$$

In analogy with the conventional fundamental equation for three-dimensional systems, we can derive the Maxwell relations from the second-order differentiations of the internal energy:

$$\left(\frac{\partial T}{\partial L}\right)_{S,N} = \left(\frac{\partial f}{\partial S}\right)_{L,N},$$
$$\left(\frac{\partial T}{\partial N}\right)_{L,S} = \left(\frac{\partial \mu}{\partial S}\right)_{L,N},$$
$$\left(\frac{\partial f}{\partial N}\right)_{L,S} = \left(\frac{\partial \mu}{\partial L}\right)_{N,S}.$$

Problem 1.5 Two-dimensional models are often used to describe the thermodynamics of molecular adsorption from a gas or a liquid solution on planar surfaces. For a one-component two-dimensional system, the fundamental equation is given by

$$dU = TdS - \varsigma dA + \mu dN,$$

where ς stands for surface pressure. Derive the Gibbs adsorption isotherm:

$$\left(\frac{\partial \varsigma}{\partial \mu}\right)_T = \frac{N}{A}.$$

Can you extend the Gibbs adsorption isotherm to multicomponent systems? What is the surface pressure if there is no adsorption?

Solution

For this system, the integrated form of the fundamental equation is

$$U = TS - \varsigma A + \mu N.$$

In comparison with its differential form, we can derive the Gibbs–Duhem equation for the two-dimensional system

$$SdT - Ad\varsigma + Nd\mu = 0.$$

At constant temperature, $SdT = 0$, thus

$$\left(\frac{\partial \varsigma}{\partial \mu}\right)_T = \frac{N}{A}.$$

For multicomponent systems, the Gibbs–Duhem equation becomes

$$SdT - Ad\varsigma + \sum_i N_i d\mu_i = 0.$$

In this case, the Gibbs adsorption isotherm becomes

$$\left(\frac{\partial \varsigma}{\partial \mu_i}\right)_{T,\mu_{j\neq i}} = \frac{N_i}{A}.$$

If there is no adsorption, $N_i = 0$ and the surface pressure vanishes, i.e., $\varsigma = 0$.

Problem 1.6 Consider gas adsorption on a planar surface at temperature T. Assume that the gas phase is ideal and that the adsorption can be described by Henry's law

$$N/A = k_H P,$$

where N is the number of gas molecules at the surface, A is the surface area, and k_H is Henry's constant. Show that the surface pressure is given by

$$\varsigma A = N k_B T,$$

where k_B is Boltzmann's constant.

Solution
For an ideal gas in the bulk, the chemical potential depends on pressure P

$$\mu = \mu_0 + k_B T \ln(P/P_0),$$

where μ_0 is the chemical potential of the ideal gas at system temperature and a reference pressure $P_0 = 1$ atm, P and P_0 take the same units.
The combination of the Gibbs isotherm with Henry's law predicts

$$\left(\frac{\partial \varsigma}{\partial \mu}\right)_T = \frac{N}{A} \Rightarrow \frac{1}{k_B T}\left(\frac{\partial \varsigma}{\partial \ln P}\right)_T = k_H P \Rightarrow \frac{1}{k_B T}\left(\frac{\partial \varsigma}{\partial P}\right)_T = k_H \Rightarrow \left(\frac{\partial \varsigma}{\partial P}\right)_T = k_H k_B T.$$

With the boundary condition $\varsigma = 0$ at $P = 0$, integrating the above equation leads to

$$\int_0^P \left(\frac{\partial \varsigma}{\partial P}\right)_T dP = \int_0^P k_H k_B T dP \Rightarrow \varsigma = k_H P k_B T.$$

Using Henry's law $N/A = k_H P$ again, we obtain an analog of the ideal-gas law for two dimensional systems,

$$\varsigma A = N k_B T.$$

Problem 1.7 Consider molecular adsorption from a liquid solution on a planar surface of area A and temperature T. Assume that the liquid phase is an ideal solution and that the adsorption of the solute molecules can be described by Henry's law

$$N/A = k_H C,$$

where N is the *moles* of solute molecules at the surface, k_H is Henry's constant, and C stands for the *molar* concentration of the solute molecules in the bulk solution. Show that the surface pressure is given by

$$\varsigma A = NRT,$$

where R is the gas constant.

Solution
The chemical potential of solute molecules in an ideal solution can be written as

$$\mu = \mu_0 + RT \ln(C/C_0),$$

where μ_0 is the chemical potential of the solute at a reference state of system temperature and $C_0 = 1$ mol/L. With Henry's law $N/A = k_H C$, the Gibbs isotherm predicts

$$\left(\frac{\partial \varsigma}{\partial \mu}\right)_T = \frac{N}{A} \Rightarrow \frac{1}{RT}\left(\frac{\partial \varsigma}{\partial \ln C}\right)_T = k_H C \Rightarrow \frac{1}{RT}\left(\frac{\partial \varsigma}{\partial C}\right)_T = k_H \Rightarrow \left(\frac{\partial \varsigma}{\partial C}\right)_T = k_H RT.$$

With the boundary condition $\varsigma = 0$ at $C = 0$, integrating the above equation leads to

$$\int_0^C \left(\frac{\partial \varsigma}{\partial C}\right)_T dC = \int_0^P k_H RT dC \Rightarrow \varsigma = k_H CRT.$$

Using Henry's law again, we obtain a two-dimensional analog of the ideal-gas law for the surface pressure

$$\varsigma A = NRT.$$

Problem 1.8 Consider ideal-gas adsorption on a planar surface such that gas molecules at the surface follows a two-dimensional equation of state

$$\varsigma(a - a_0) = k_B T,$$

where a is the surface area per molecule, and a_0 is the surface area occupied by each molecule. Show that the adsorption isotherm follows the Volmer isotherm

$$Pk_H = \frac{\theta}{1-\theta} \exp\left(\frac{\theta}{1-\theta}\right),$$

where $\theta = a_0/a$ stands for the surface coverage, and k_H is Henry's constant defined by $k_H = \theta/P$ as $P \to 0$. How would you extend the Volmer equation to adsorption on a planar surface from an ideal solution?

Solution

For an ideal gas at constant temperature T, the chemical potential varies with the bulk pressure P

$$d\mu = k_B T d \ln P.$$

The two-dimensional equation of state predicts that the surface pressure varies with the surface area per molecule

$$d\varsigma = -k_B T \frac{da}{(a - a_0)^2}.$$

Substituting these two equations into the Gibbs isotherm (Problem 1.5) yields

$$\left(\frac{\partial \varsigma}{\partial \mu}\right)_T = \frac{N}{A} \Rightarrow -\frac{1}{(a-a_0)^2}\left(\frac{\partial a}{\partial \ln P}\right)_T = \frac{1}{a}.$$

Integrating the above equation leads to

$$-\int_\infty^a \frac{a}{(a-a_0)^2} da = \int_0^P d \ln P \Rightarrow -\ln(a - a_0) + \frac{a_0}{a - a_0} = \ln P + K,$$

where K is an integration constant. Replacing a_0/a with θ gives

$$-\ln\left(\frac{1-\theta}{\theta}\right) + \frac{\theta}{1-\theta} = \ln(Pa_0) + K. \tag{A}$$

The integration constant can be fixed with the boundary condition $\theta = k_H P$ as $P \to 0$,

$$K = \ln(k_H/a_0).$$

Substituting K into Eq. (A) leads to the Volmer equation

$$Pk_H = \frac{\theta}{1-\theta}\exp\left(\frac{\theta}{1-\theta}\right).$$

For adsorption from an ideal solution, we replace P with the molar concentration of the solute

$$d\mu = k_B T d\ln C,$$

which leads to

$$Ck_H = \frac{\theta}{1-\theta}\exp\left(\frac{\theta}{1-\theta}\right),$$

where $\theta = a_0/a = k_H C$ as $C \to 0$.

Problem 1.9 Consider ideal-gas adsorption on a planar surface such that gas molecules at the surface follows a two-dimensional analog of the van der Waals equation of state

$$\varsigma = k_B T/(a-a_0) - c/a^2,$$

where a is the surface area per molecule, a_0 is the surface area occupied by each molecule, and c is an energy parameter that accounts for the intermolecular attraction at the surface. Show that the adsorption isotherm follows the Hill–Deboer equation

$$\ln\left[\frac{P(1-\theta)}{\theta}\right] - \frac{\theta}{1-\theta} = -\ln K_1 - \frac{K_2\theta}{k_B T},$$

where $\theta = a_0/a$ stands for the surface coverage, K_1 is defined by $K_1 = \theta/P$ as $P \to 0$ (viz., Henry's constant), and $K_2 = 2c/a_0$.

Solution

For an ideal gas at constant temperature T, the chemical potential varies with the bulk pressure P

$$d\mu = k_B T d\ln P.$$

The van der Waals-like equation predicts that the surface pressure varies with the surface area per molecule

$$d\varsigma = -k_B T\frac{da}{(a-a_0)^2} + \frac{2c}{a^3}da.$$

Substituting these two equations into the Gibbs isotherm gives (Problem 1.5)

$$\left(\frac{\partial\varsigma}{\partial\mu}\right)_T = \frac{N}{A} \Rightarrow \left[-\frac{1}{(a-a_0)^2} + \frac{2c}{k_B T a^3}\right]\left(\frac{\partial a}{\partial \ln P}\right)_T = \frac{1}{a}.$$

Integrating the above equation leads to

$$-\int_\infty^a \frac{a}{(a-a_0)^2}da + \int_\infty^a \frac{2c}{k_B T a^2}da = \int_0^P \ln P dP \Rightarrow$$
$$-\ln(a-a_0) + \frac{a_0}{a-a_0} - \frac{2c}{k_B T a} = \ln P + K,$$

where K is an integration constant. Replacing a_0/a with θ gives

$$-\ln\left(\frac{1-\theta}{\theta}\right) + \frac{\theta}{1-\theta} - \frac{2c\theta}{k_B T a_0} = \ln(Pa_0) + K, \tag{B}$$

where the integration constant can be fixed with the boundary condition $\theta = K_1 P$ as $P \to 0$,

$$K = \ln(K_1/a_0).$$

The Hill–Deboer isotherm is obtained by substituting K into Eq. (B)

$$\ln\left[\frac{P(1-\theta)}{\theta}\right] - \frac{\theta}{1-\theta} = -\ln K_1 - \frac{K_2\theta}{k_B T},$$

where $K_2 = 2c/a_0$.

Problem 1.10 A container includes a large number of gas molecules that do not interact with each other. Assume that the container wall is elastic and that the gas molecules can be represented by non-interacting classical particles. Does the system satisfy the ergodic hypothesis? Why?

Solution
For non-interacting classical particles in an elastic container, the kinetic energy is fixed by the initial condition. Because microstates in the ensemble are not mutually accessible to each other, the system is non-ergodic.

Problem 1.11 The Gibbs equation for entropy can be derived from the hypothesis that entropy is an ensemble average of some microscopic property depending only on the microstate probability, i.e.,

$$S = \sum_{\nu} p_{\nu} f(p_{\nu}),$$

where $f(p_\nu)$ may be understood as the microscopic counterpart of entropy at microstate ν. Show that this hypothesis leads to $f(p_\nu) = -k_B \ln p_\nu$. [Hint: Consider entropy additivity for independent thermodynamic systems.]

Solution
Consider the total entropy S_T of two independent systems A and B. Because entropy is extensive (viz., additivity), S_T can be written as

$$S_T = S_A + S_B,$$

where S_A and S_B are the entropies of individual systems. The microstate of the entire system is the sum of those corresponding to systems A and B, $\nu_T = \nu_A + \nu_B$. Because systems A and B are independent, the joint probability p_{ν_T} is a product of p_{ν_A} and p_{ν_B}, the microstate probabilities of individual systems,

$$p_{\nu_T} = p_{\nu_A} p_{\nu_B}.$$

If the entropy corresponds to an ensemble average of some microscopic property depending only on the microstate probability, we have

$$S_T = \sum_{\nu_T} p_{\nu_T} f(p_{\nu_T}) = \sum_{\nu_A}\sum_{\nu_B} p_{\nu_A} p_{\nu_B} f(p_{\nu_A} p_{\nu_B})$$

and

$$S_A + S_B = \sum_{\nu_A} p_{\nu_A} f(p_{\nu_A}) + \sum_{\nu_B} p_{\nu_B} f(p_{\nu_B}) = \sum_{\nu_A}\sum_{\nu_B} p_{\nu_A} p_{\nu_B} [f(p_{\nu_A}) + f(p_{\nu_B})],$$

where the second equal sign follows the probability normalization conditions,

$$\sum_{\nu_A} p_{\nu_A} = \sum_{\nu_B} p_{\nu_B} = 1.$$

Because the microstate distributions p_{ν_A} and p_{ν_B} are arbitrary, the entropy additivity requires

$$f(p_{\nu_A} p_{\nu_B}) = f(p_{\nu_A}) + f(p_{\nu_B}). \tag{C}$$

Differentiating both sides of Eq. (C) with respect to p_{ν_A} at fixed p_{ν_B} leads to

$$\frac{\partial f(p_{\nu_A}p_{\nu_B})}{\partial p_{\nu_A}} = \frac{\partial f(p_{\nu_A}p_{\nu_B})}{\partial p_{\nu_A}p_{\nu_B}}p_{\nu_B} = \frac{\partial f(p_{\nu_A})}{\partial p_{\nu_A}}. \tag{D}$$

Similarly, differentiation of Eq. (C) with respect to p_{ν_B} at constant p_{ν_A} gives

$$\frac{\partial f(p_{\nu_A}p_{\nu_B})}{\partial p_{\nu_B}} = \frac{\partial f(p_{\nu_A}p_{\nu_B})}{\partial p_{\nu_A}p_{\nu_B}}p_{\nu_A} = \frac{\partial f(p_{\nu_B})}{\partial p_{\nu_B}}. \tag{E}$$

A comparison of Eqs. (D) and (E) yields

$$p_{\nu_A}\frac{\partial f(p_{\nu_A})}{\partial p_{\nu_A}} = p_{\nu_B}\frac{\partial f(p_{\nu_B})}{\partial p_{\nu_B}}. \tag{F}$$

Because systems A and B are arbitrary, Eq. (F) suggests

$$\frac{\partial f(p_\nu)}{\partial \ln p_\nu} = K, \tag{G}$$

where K is a system-independent constant. Integration of Eq. (G) gives

$$f(p_\nu) = K\ln p_\nu + K', \tag{H}$$

where K' is an integration constant. In Eq. (H), entropy additivity requires $K' = 0$, and the universal constant K is not essential in the definition of the entropy (e.g., it was set as one in information entropy). In comparison with classical thermodynamics, it can be identified as $K = k_B$ by applying the Gibbs entropy to an ideal-gas system.

Problem 1.12 Suppose that a thermodynamic system has an initial distribution of microstates specified by $\{p_\nu^0\}$, where ν denotes microstates, and reaches a new microstate distribution $\{p_\nu\}$ at equilibrium. Show that

$$\sum_\nu p_\nu \ln p_\nu \geq \sum_\nu p_\nu \ln p_\nu^0,$$

where the equality holds if and only if $p_\nu = p_\nu^0$ for all ν. [Hint: $\ln x \leq x - 1$ for all $x > 0$ with equality if and only if $x = 1$.]

Solution

Using $\ln x \leq x - 1$ for all $x > 0$, we can prove the inequality by rearranging the terms

$$\sum_\nu p_\nu \ln(p_\nu^0/p_\nu) \leq \sum_\nu p_\nu(p_\nu^0/p_\nu - 1) = \sum_\nu p_\nu^0 - \sum_\nu p_\nu = 1 - 1 = 0.$$

Because $\ln x = x - 1$ only at $x = 1$, the equal sign holds if and only if $p_\nu = p_\nu^0$.

Problem 1.13 Consider a lattice model for a one-component gas such that each site can accommodate no more than one gas molecule. Assume that each microstate of the system is defined by a particular occupation of the lattice sites by the gas molecules.

(i) What is the number of microstates for the lattice system with n-sites containing N gas molecules?

(ii) Show that the lattice model predicts an entropy

$$S = -nk_B\left[x\ln x + (1-x)\ln(1-x)\right],$$

where $x = N/n$. [Hint: $\ln n! \approx n\ln n - n$.]

(iii) Assume that the system volume is proportional to the number of lattice sites, i.e., $V = nv_0$, where v_0 is the volume for each site. Show that, when $x \to 0$ (i.e., low gas density), the entropy change in response to the volume change from V_1 to V_2 is

$$\Delta S = Nk_B \ln(V_2/V_1).$$

(iv) Show that, when $x \to 0$, the lattice model satisfies the ideal-gas law $PV = Nk_BT$.

(v) How does the entropy change with temperature according to this model?

Solution

(i) The number of microstates for the lattice system is given by the number of combinations:

$$W = \binom{n}{N} = \frac{n!}{N!(n-N)!}.$$

(ii) The entropy is given by the Boltzmann equation

$$S/k_B = \ln W = \ln n! - \ln N! - \ln(n-N)!.$$

Using the Stirling approximation $\ln n! \approx n \ln n - n$, we can rewrite the above equation as

$$S/k_B = -N \ln(N/n) - (n-N) \ln(n-N)/n = -n\left[x \ln x + (1-x) \ln(1-x)\right],$$

where $x = N/n$.

(iii) When $x \to 0$, $|\ln x| \gg 1$, the system entropy becomes

$$S = -nk_B\left[x \ln x + (1-x) \ln(1-x)\right] \approx -Nk_B \ln(N/n).$$

Because the system volume is proportional to the number of lattice sites, we have $n = V/v_0$, where v_0 is the volume per lattice site. The above equation becomes

$$S = -Nk_B \ln(Nv_0/V). \tag{I}$$

Eq. (I) predicts that a change in volume from V_1 to V_2 at constant N leads to the entropy change

$$\Delta S = Nk_B \ln(V_2/V_1).$$

(iv) The Maxwell relation indicates

$$\left(\frac{\partial P}{\partial T}\right)_{V,N} = \left(\frac{\partial S}{\partial V}\right)_{T,N}.$$

According to Eq. (I)

$$\left(\frac{\partial S}{\partial V}\right)_{T,N} = \frac{Nk_B}{V}.$$

Using the boundary condition $P = 0$ as $T \to 0$, we obtain the ideal-gas law $PV = Nk_BT$ by integrating

$$\left(\frac{\partial P}{\partial T}\right)_{V,N} = \frac{Nk_B}{V}$$

with respect to T at constant V and N.

(v) This lattice model predicts that entropy does not change with temperature (Eq. I). In comparison with a real gas, the erroneous prediction can be attributed to the neglect of molecular energy.

Problem 1.14 Consider a lattice model for a one-component gas such that each lattice site can accommodate no more than one gas molecule. Each gas molecule on the lattice is able to take m orientations with equal energy. Assume that the system volume is proportional to the number of lattice sites, $V = nv_0$, where n is the number of lattice sites, and v_0 is the volume per lattice site.

(i) What is the entropy of the system in terms of the number of gas molecules N and the total number of lattice sites n.

(ii) Show that, when $x = N/n \to 0$ (i.e., low gas density), the entropy change in response to the volume change from V_1 to V_2 is

$$\Delta S = Nk_B \ln(V_2/V_1).$$

(iii) Show that, when $x \to 0$, the lattice model satisfies the ideal-gas law $PV = Nk_BT$.

Solution

(i) According to this model, each microstate is defined by a particular occupation of the lattice sites and the orientations of the gas molecules

$$W = \binom{n}{N} m^N = \frac{n!}{N!(n-N)!} m^N.$$

The Boltzmann equation predicts that the entropy is

$$\begin{aligned} S/k_B &= \ln W = \ln n! - \ln N! - \ln(n-N)! + N \ln m \\ &= -n\,[x \ln x + (1-x)\ln(1-x)] + N \ln m, \end{aligned}$$

where $x = N/n$.

(ii) When $x \to 0$, $|\ln x| \gg 1$, the system entropy becomes

$$S = -nk_B\,[x \ln x + (1-x)\ln(1-x) + N \ln m] \approx -Nk_B \ln(N/n) + Nk_B \ln m.$$

Because the system volume is proportional to the number of lattice sites, we have $n = V/v_0$, where v_0 is the volume per lattice site. The above equation becomes

$$S = -Nk_B \ln(Nv_0/V) + Nk_B \ln m. \tag{J}$$

Eq. (J) predicts that a change in volume from V_1 to V_2 at constant N leads to the entropy change

$$\Delta S = Nk_B \ln(V_2/V_1).$$

This problem affirms that entropy is a relative quantity, i.e., grouping m independent orientations for each molecule into one "coarse-grained" state does not change the relative entropy.

(iii) Following the Maxwell relation

$$\left(\frac{\partial P}{\partial T}\right)_{V,N} = \left(\frac{\partial S}{\partial V}\right)_{T,N},$$

and Eq. (J) for

$$\left(\frac{\partial S}{\partial V}\right)_{T,N} = \frac{Nk_B}{V},$$

we can obtain the ideal-gas law $PV = Nk_BT$ by integrating

$$\left(\frac{\partial P}{\partial T}\right)_{V,N} = \frac{Nk_B}{V}$$

with respect to T at constant V and N and the boundary condition $P = 0$ as $T \to 0$.

Problem 1.15 Repeat Problem 1.14 by assuming that the gas molecules do not interact with each other and that the m-orientations for each gas molecule on the lattice have different energies $\epsilon_i, i = 1,2,\ldots,m$. How does the molecular orientation influence the relative entropy of the system?

Solution

(i) Each microstate is still defined by a particular occupation of the lattice sites and the orientation of the gas molecules. If the gas molecules do not interact completely, we cannot keep track of whether each site is occupied or empty. Therefore,

$$W = \frac{n^N}{N!}\mathfrak{m}^N.$$

where $\mathfrak{m}$ is the number of *accessible* orientations. In general, $\mathfrak{m}$ depends on the system temperature and may not be the same as m.
The entropy is then given by

$$S/k_B = \ln W = N\ln(n\mathfrak{m}) - \ln N! = N[\ln(n\mathfrak{m}/N) + 1].$$

(ii) When $x = N/n \to 0$, $|\ln x| \gg 1$, the equation for entropy remains the same because the molecules do not interact

$$S/k_B = N[\ln(n\mathfrak{m}/N) + 1].$$

If the system volume is proportional to the number of lattice sites, we have $n = V/v_0$, where v_0 is the volume per lattice site. The above equation becomes

$$S = -Nk_B\ln(Nv_0/V) + Nk_B(\ln\mathfrak{m} + 1). \tag{K}$$

Eq. (K) predicts that a change in volume from V_1 to V_2 at constant N leads to the entropy change

$$\Delta S = Nk_B\ln(V_2/V_1).$$

Again, entropy is a relative quantity, i.e., grouping m independent orientations for each molecule into one "coarse-grained" state does not change the relative entropy.

(iii) Following the Maxwell relation

$$\left(\frac{\partial P}{\partial T}\right)_{V,N} = \left(\frac{\partial S}{\partial V}\right)_{T,N},$$

and Eq. (K) for

$$\left(\frac{\partial S}{\partial V}\right)_{T,N} = \frac{Nk_B}{V},$$

we can thus obtain the ideal-gas law $PV = Nk_BT$ by integrating

$$\left(\frac{\partial P}{\partial T}\right)_{V,N} = \frac{Nk_B}{V}$$

with respect to T at constant V and N and the boundary condition $P = 0$ as $T \to 0$.

Because the gas molecules do not interact with each other, the molecular orientations may be considered as the internal degrees of freedom, which make only a fixed contribution to the total entropy ($Nk_B\ln\mathfrak{m}$) but have no effect on the relative entropy.

Problem 1.16 Consider a lattice model such that each site can be in one of two energy states, 0 or $\epsilon > 0$. Let n be the total number of lattice sites, and N the number of sites with energy ϵ.

(i) How would you define the microstates of this system?
(ii) Show that the lattice sites with different energies follow the Boltzmann distribution

$$\frac{N}{n-N} = \exp\left(-\frac{\epsilon}{k_B T}\right).$$

(iii) Show that the constant-volume heat capacity of the lattice system is given by

$$C_V = \frac{N(n-N)}{n}\frac{\epsilon^2}{k_B T^2}.$$

(iv) Can the absolute temperature be negative? Why?

Solution

(i) For this system, each microstate is defined by the energies of individual lattice sites.
(ii) The system temperature can be found from the fundamental equation

$$\frac{1}{T} = \left(\frac{\partial S}{\partial U}\right)_V, \tag{L}$$

where $V = nv_0$. The entropy of the lattice system is

$$S/k_B = -N\ln(N/n) - (n-N)\ln(n-N)/n,$$

and the internal energy is

$$U = N\epsilon.$$

Because

$$\left(\frac{\partial S}{\partial U}\right)_V = \frac{1}{\epsilon}\left(\frac{\partial S}{\partial N}\right)_V = \frac{1}{\epsilon}\left(\frac{\partial S}{\partial N}\right)_n = -\frac{k_B}{\epsilon}\ln\left(\frac{N}{n-N}\right).$$

Substituting the above equation into Eq. (L) yields

$$\frac{N}{n-N} = \exp\left(-\frac{\epsilon}{k_B T}\right).$$

(iii) The constant-volume heat capacity is defined as

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V.$$

Because $U = \epsilon N$ and $V = nv_0$, the heat capacity of this system becomes

$$C_V = \epsilon\left(\frac{\partial N}{\partial T}\right)_n.$$

Noting

$$N = \frac{n}{1+\exp\left(\frac{\epsilon}{k_B T}\right)},$$

we have

$$\left(\frac{\partial N}{\partial T}\right)_n = \frac{n\exp\left(\frac{\epsilon}{k_B T}\right)}{\left[1+\exp\left(\frac{\epsilon}{k_B T}\right)\right]^2}\frac{\epsilon}{k_B T^2} = \frac{N(n-N)}{n}\frac{\epsilon}{k_B T^2}.$$

Thus

$$C_V = \frac{N(n-N)}{n}\frac{\epsilon^2}{k_B T^2}.$$

(iv) According to this model, the absolute temperature is negative when $N > n - N$ (see part ii). Negative temperature is possible because, under such conditions, the entropy falls as the system energy increases. The possibility of negative absolute temperatures was first proposed by Lars Onsager.[1]

Problem 1.17 Imagine that Maxwell's demon could control the direction of molecules passing through a hole between identical chambers A and B containing a one-component ideal gas. The demon allows all molecules, fast or slow, to pass from B to A but prevent them from passing from A to B. Eventually all molecules will be concentrated in A and a vacuum will be created in B so that a pressure difference is generated without doing any work. Explain whether the process violates the first or the second law of thermodynamics and discuss how this might be implemented with modern technology.

Solution
The system temperature is invariant during this process because the demon manipulates only the locations of ideal gas molecules without altering the molecular velocities. Overall, there is no change in the internal energy of the system. The entropy change for the compression of the ideal gas is

$$\Delta S = k_B N \ln(V/2V) = -Nk_B \ln 2,$$

where N is the number of gas molecules, and V is the volume for each chamber. The reduction of entropy, ΔS, is attributed to the information gained by the demon in recognizing the direction of each gas molecule

$$S_{info} = k_B \ln 2^N = Nk_B \ln 2.$$

Therefore, neither the first nor the second law was violated. Useful energy can be acquired if a device could distinguish the direction of molecular motions at any instant.[2]

Problem 1.18 In a computer, the Memory Address Register (MAR) is responsible for storing either the memory address from which data will be fetched to the Central Processing Unit (CPU), or the address to which data will be sent and stored. Consider a computer operation that reformats a memory register of n bits. Before the operation, the register as a whole could have existed in any of 2^n states. However, after the operation, the register is left in only one state. To maintain the temperature of the computer at this point, how much heat must be released?

Solution
The operation compressed 2^n logical states into one, leading to the reduction of entropy $\Delta S = -nk_B \ln 2$. The heat dissipated satisfies the Clausius inequality $\Delta S \geq Q/T$, i.e., the minimum heat released is $Q_{min} = nk_B T \ln 2$.

1 Onsager, L., "Statistical Hydrodynamics", *Il Nuovo Cimento*, 6: 279–287 (1949).
2 Toyabe S., Sagawa T., Ueda M. et al., "Experimental demonstration of information-to-energy conversion and validation of the generalized Jarzynski equality", *Nature Phys*., 6, 988–992 (2010).