Grading policy: One point is given for each numbered equation shown in the solution, or for written state-
ments and/or equations to the same effect. The total score for this problem set is 20 points with a maximum
of 2 bonus points awardable in Problem 2.

1. Calculate the value of the pressure (in atm) exerted by a 33.9-foot column of water. Take the density of
water to be 1.00 g · mL⁻¹. [5 points]

Solution. Plug the numbers into the equation for hydrostatic pressure:

\[ P = \rho gh \]

\[ = (1.00 \text{ g} \cdot \text{mL}^{-1}) \cdot (33.9 \text{ ft} \times 0.305 \text{ m} \cdot \text{ft}^{-1}) \cdot (9.81 \text{ m} \cdot \text{s}^{-2}) \]

\[ = (1.00 \times 10^3 \text{ kg} \cdot \text{m}^{-3}) \cdot (34.32 \text{ m} \cdot \text{s}^{-2}) \]

\[ = 101 \text{ kPa} \times 0.987 \times 10^{-3} \text{ atm} \cdot \text{kPa}^{-1} \]

\[ = 1.00 \text{ atm} \]

Common mistake: Many people did not keep track of significant figures. An answer of 1 atm was not
accepted.

2. Show that the Lennard-Jones potential can be written as

\[ u(r) = \varepsilon \left( \frac{r^*}{r} \right)^{12} - 2\varepsilon \left( \frac{r^*}{r} \right)^6 \]  

where \( r^* \) is the value of \( r \) at which \( u(r) \) is a minimum. [3 + 2 points]

Solution. The form of the Lennard-Jones potential given in the book (Eq. 16.29, last line of p. 661) is

\[ u(r) = 4\varepsilon \left[ \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^6 \right] \]

To express \( r^* \) in terms of \( \sigma \), we differentiate (7) to find the stationary point. [1 bonus point was
awarded for this derivation and 1 point for the final answer]

\[ u'(r) = 24\varepsilon \left[ -2 \left( \frac{\sigma^{12}}{r^{13}} \right) + \left( \frac{\sigma^6}{r^7} \right) \right] = \frac{24\varepsilon}{r} \left( \frac{\sigma}{r} \right)^6 \left[ 1 - 2 \left( \frac{\sigma}{r} \right)^6 \right] \]

\[ u'(r) = 0 \iff r = \sigma \sqrt[6]{2} \]

\[ r = 2^{1/6} \sigma \]

1
Testing the nature of the stationary point, the first derivative test is applied: [1 bonus point for applying any test]

\[ u'(6\sqrt{2}\sigma \pm \delta) = \frac{24\varepsilon}{6\sqrt{2}\sigma \pm \delta} \left( \frac{\sigma}{6\sqrt{2}\sigma \pm \delta} \right)^6 \left[ 1 - 2 \left( \frac{\sigma}{6\sqrt{2}\sigma \pm \delta} \right)^6 \right] \]

\[ \approx \frac{24\varepsilon}{6\sqrt{2}\sigma} \left( \frac{1}{2} \right) \left[ 1 - \left( 1 \pm \frac{\delta}{6\sqrt{2}\sigma} \right)^{-6} \right] \]

\[ \approx \frac{12\varepsilon}{6\sqrt{2}\sigma} \left[ 1 - \left( 1 \pm \frac{6\delta}{6\sqrt{2}\sigma} \right) \right] = \mp \frac{72\varepsilon\delta}{3\sqrt{2}\sigma^2} \]

Since \( \varepsilon \) is positive and \( \sigma \) is real,

\[ u'(6\sqrt{2}\sigma - \delta) > 0 > u'(6\sqrt{2}\sigma + \delta) \quad (10) \]

and therefore the stationary point is a minima. This is confirmed from the graph (Fig. 16.13, p. 662).

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3. Prove that the second virial coefficient calculated from a general intermolecular potential of the form

\[ u(r) = (\text{energy parameter}) \times f \left( \frac{r}{\text{distance parameter}} \right) \quad (11) \]

rigorously obeys the law of corresponding states. Does the Lennard-Jones potential satisfy this condition? [6 points]

Solution. The second virial coefficient \( B_{2V}(T) \) is related to \( u(r) \) by Eq. 16.25 (p. 660):

\[ B_{2V}(T) = -2\pi N_A \int_{0}^{+\infty} \left[ e^{-\frac{u(r)}{k_BT}} - 1 \right] r^2 dr \quad (12) \]

Denoting the energy parameter by \( \varepsilon \) and the distance parameter by \( \rho \), the potential is then

\[ u(r) = \varepsilon f \left( \frac{r}{\rho} \right) \quad (13) \]

Substituting (13) into (12) gives

\[ B_{2V}(T) = -2\pi N_A \int_{0}^{+\infty} \left[ e^{-\frac{\varepsilon f(z)}{k_BT}} - 1 \right] z^2 dz \quad (14) \]

To obtain the law of corresponding states, all the quantities appearing in (12) must be expressed in reduced variables, i.e., as dimensionless quantities. In (14) the argument of the exponent can be seen to be dimensionless since both \( \varepsilon \) and \( k_BT \) have dimensions of energy. Also, both \( r \) and \( \rho \) have dimensions of length, so any function of \( \frac{r}{\rho} \) must also be dimensionless to be dimensionally correct. Introducing \( R = \frac{z}{\rho} \) into (14) gives

\[ B_{2V}(T) = -2\pi N_A \rho^3 \int_{0}^{+\infty} \left[ e^{-\frac{\varepsilon f(z)}{k_BT}} - 1 \right] R^2 dR \quad (15) \]

But from the original equation (12) it is clear that the (SI) units of \( B_{2V} \) are \( \text{m}^3 \cdot \text{mol}^{-1} \), and therefore \( B_{2V} \) has the same dimensions as the quantity \(-2\pi N_A \rho^3\). Dividing both sides of (15) by this quantity therefore yields

\[ B^*_{2V}(T) = -\frac{B_{2V}(T)}{2\pi N_A \rho^3} = \int_{0}^{+\infty} \left[ e^{-\frac{\varepsilon f(z)}{k_BT}} - 1 \right] R^2 dR \quad (16) \]

which is dimensionless throughout and therefore obeys the law of corresponding states.
Common mistakes:

- Writing a reduced temperature $\tau$ is also acceptable. However, the parameter of $B_{2V} (T)$ should change to become $B_{2V} (\tau)$.
- Some people misinterpreted the intermolecular potential given to mean

$$u(r) = \varepsilon f \times \left( \frac{r}{\rho} \right) = \frac{\varepsilon f r}{p}$$

which is incorrect. The parentheses () state the parameter(s) of the function and do not represent multiplication.

The Lennard Jones potential (6) can be written in the form

$$u(r) = \varepsilon \left[ \left( \frac{r}{r^*} \right)^{12} - 2 \left( \frac{r}{r^*} \right)^6 \right]$$

which is of the form (13) with

$$R = \frac{r^*}{r} \quad (17)$$
$$f(R) = R^{12} - 2R^6 \quad (18)$$

From the previous part of the problem the result follows that the Lennard-Jones potential obeys the law of corresponding states.

**Note.** $R = \frac{r^*}{r}$ is also acceptable, but the function must be identified as $f(R) = R^{-12} - 2R^{-6}$.

4. The coefficient of thermal expansion $\alpha$ is defined as

$$\alpha = \frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_P \quad (19)$$

Show that

$$\alpha = \frac{1}{T} \quad (20)$$

for an ideal gas. [3 points]

**Solution.** The ideal gas equation states that $P\tilde{V} = RT$, or

$$\tilde{V} = \frac{RT}{P} \quad (21)$$

Taking the partial derivative with respect to $T$ (keeping $P$ constant) gives

$$\left( \frac{\partial \tilde{V}}{\partial T} \right)_P = \frac{R}{P} \quad (22)$$

Substituting (21) and (22) into (19) gives

$$\alpha = \frac{P}{RT} \cdot \frac{R}{P} = \frac{1}{T} \quad (23)$$
5. The isothermal compressibility $\kappa$ is defined as

$$\kappa = -\frac{1}{V} \left( \frac{\partial V}{\partial P} \right)_T$$

(24)

Show that

$$\kappa = \frac{1}{P}$$

(25)

for an ideal gas. [3 points]

**Solution.** The ideal gas equation states that $PV = RT$, or

$$\tilde{V} = \frac{RT}{P}$$

(26)

Taking the partial derivative with respect to $P$ (keeping $T$ constant) gives

$$\left( \frac{\partial \tilde{V}}{\partial P} \right)_T = -\frac{RT}{P^2}$$

(27)

Substituting (26) and (27) into (24) gives

$$\kappa = -\frac{P}{RT} \cdot -\frac{RT}{P^2} = \frac{1}{P}$$

(28)