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Prediction of the Attractive Branch of the Effective Pair Potential Using the Joule–Thomson Inversion Curve

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In the present work, the attractive branch of the effective pair potential is predicted by using p-v-T data of the Joule–Thomson inversion curve. It is concluded that all loci of the thermodynamic states of the inversion curve correspond to the attractive branch of the effective pair potential. It is also predicted that the minimum of the effective pair potential well, r_m, is less than that of the isolated pair potential, because the attraction term has a longer range than the repulsion term.

KEY WORDS: effective pair potential; inversion curve; Joule–Thomson coefficient.

1. INTRODUCTION

An important concept in physical chemistry concerns the representation of the force between two molecules by means of a potential energy function. In dense systems this is complex, because a molecule in a condensed phase is at all times close to several other molecules. The total intermolecular energy is consequently large, and the properties of these states depend strongly on the nature of the intermolecular forces. When several molecules are simultaneously close to each other, their total energy is not exactly equal to the sum of the pair energies, which would be observed if each pair were isolated. Due to the fact that the relations between the forces and the bulk properties are known in principle, it is clear that the study of dense systems can provide valuable information about the intermolecular interactions. However, the relation between the intermolecular potential and the

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measurable properties of a fluid is quite complex. Only a few experimental methods are available for a determination of the molecular interactions. The most direct method is molecular-beam scattering by which the repulsive term can be obtained [1].

Bulk properties of gases such as the second virial coefficient, B_2, the viscosity, and the Joule–Thomson coefficient, $\mu_{\text{J–T}}$, are related to the intermolecular forces. Unfortunately, B_2 is not very sensitive to the form of the intermolecular potential, whereas $\mu_{\text{J–T}}$ is more sensitive than the second viral coefficient. The Joule–Thomson coefficient in the zero-pressure limit can yield useful information on the nature of the intermolecular forces [2].

The main objective of this work is to use p–v–T data of the inversion curve to predict the effective pair potential. We first give a brief review of the properties of the inversion curve and then calculate the potential.

2. THE JOULE–THOMSON INVERSION CURVE

The Joule–Thomson coefficient, $\mu_{\text{J–T}}$, is defined by the relation,

$$\mu_{\text{J–T}} = (\partial T/\partial p)_H \tag{1}$$

By using the exact thermodynamic relations, Eq. (1) may be written as

$$\mu_{\text{J–T}} = \frac{1}{C_p}\,[T(\partial v/\partial T)_p - v] \tag{2}$$

where v, T, and p are the volume, temperature, and pressure as usual, and C_p is the heat capacity at constant pressure. The inversion curve is determined by the condition, $\mu_{\text{J–T}} = 0$. There is a near-parabolic locus of points in (T, p) space enclosing a $\mu_{\text{J–T}} > 0$ (cooling on expansion) region, separating it from the region in which $\mu_{\text{J–T}} < 0$ (heating on expansion) for the rest of (T, p) space. At all pressures up to a maximum value $p_{\text{in}}^{\text{Max}}$, there are two temperatures at which $\mu_{\text{J–T}} = 0$. Using Eq. (2), the isobaric expansivity on the inversion curve is equal to $1/T[\alpha = 1/T$ or $(\partial p/\partial T)_p = -p/T]$. It is possible to rearrange Eq. (2) in the following form:

$$\mu_{\text{J–T}} = \frac{RT^2}{pC_p}\,(\partial Z/\partial T)_p \tag{3}$$

where Z is the compressibility factor. As is evident from Eq. (3), at each inversion point, $(\partial Z/\partial T)_p$ must be equal to zero. If we separate the contributions of the internal and thermal pressures $(p_{\text{in}}, p_{\text{th}})$, using $p = p_{\text{th}} - p_{\text{in}}$, in which $p_{\text{th}} = T(\partial p/\partial T)_v$ and $p_{\text{in}} = (\partial E/\partial v)_T$, the compressibility factor may be written as the algebraic sum of the thermal compressibility, Z_{th}, and the internal compressibility, Z_{in}, as

$$Z = \frac{p}{\rho RT} = \frac{p_{\text{th}} - p_{\text{in}}}{\rho RT} = Z_{\text{th}} - Z_{\text{in}} \tag{4}$$

where ρ is the molar density and RT has its usual meaning. Since at each inversion point, $(\partial Z/\partial T)_p = 0$, we may write

$$(\partial Z_{\text{th}}/\partial T)_p = (\partial Z_{\text{in}}/\partial T)_p \tag{5}$$

It means that at any inversion point, the contributions of the thermal and internal compressibility factors in $\mu_{\text{J–T}}$ cancel each other exactly.

3. PREDICTION OF THE ATTRACTIVE BRANCH OF THE EFFECTIVE PAIR POTENTIAL

In this section we want to predict the effective pair potential using the p–v–T data of the inversion curve. As we mentioned before, on the inversion curve the slope of Z with respect to temperature is equal to zero. Therefore, by using $\alpha = 1/T$, on the inversion curve, we may write

$$(\partial Z/\partial T)_p = (\partial Z/\partial \rho)_p (\partial \rho/\partial T)_p = (-\rho/T)(\partial Z/\partial \rho)_p \tag{6}$$

When

$$(\partial Z/\partial \rho)_p = 0 \tag{7}$$

differentiation of Eq. (4) gives

$$(\partial Z/\partial \rho)_p = (\partial Z_{\text{th}}/\partial \rho)_p - (\partial Z_{\text{in}}/\partial \rho)_p = 0 \tag{8}$$

Therefore, the slope of the thermal and internal compressibility factors with respect to density cancel each other exactly on the inversion curve. Now, let us calculate each term in Eq. (8) by using Eq. (4):

$$Z_{\text{in}} = (\partial E/\partial v)_T/\rho RT = -\frac{\rho}{RT}(\partial E/\partial \rho)_T \tag{9}$$

and

$$(\partial Z_{\text{in}}/\partial \rho)_p = \frac{1}{R}\left[\frac{1}{T} - \frac{\rho(\partial T/\partial \rho)_p}{T^2}\right](\partial E/\partial \rho)_T + \frac{\rho}{RT}\left[\frac{\partial(\partial E/\partial \rho)_T}{\partial \rho}\right]_p \tag{10}$$

Since the derivative of E is taken at constant T, with a good approximation we may replace the internal energy, E, with the potential, U [3]. After some algebra, we obtain

$$(\partial Z_{\text{in}}/\partial \rho)_p = -\left[\frac{2(\partial U/\partial \rho)}{RT} + \frac{\rho(\partial^2 U/\partial \rho^2)}{RT}\right] \tag{11}$$

$$= \frac{-1}{RT}[2U' + \rho U''] \tag{12}$$

where U' and U'' are the first and second derivatives of U with respect to density. The above equation is equal to $(\partial Z_{\text{th}}/\partial \rho)_p$ [see Eq. (8)], whose value can be inserted in Eq. (12). Again, from Eq. (4), we have

$$Z_{\text{th}} = \frac{(\partial p/\partial T)_\rho}{\rho R} \tag{13}$$

Therefore, we may write Eq. (12) as

$$\frac{(\rho U'' + 2U')}{RT} = \frac{(\partial p/\partial T)_\rho}{R\rho^2} \tag{14}$$

or

$$U'' + 2U'/\rho = T\,\frac{(\partial p/\partial T)_\rho}{\rho^3} \tag{15}$$

If we solve this differential equation, we can obtain the effective pair potential function. To do so, we may use the new variable, ξ, as $U' = \xi = (dU/d\rho)$; then Eq. (15) will be given by

$$\xi' + \frac{2\xi}{\rho} = \frac{T(\partial p/\partial T)_\rho}{\rho^3} \tag{16}$$

Solving Eq. (16) gives the derivative of the effective pair potential with respect to density as

$$\xi = \frac{(p + \mathrm{C})}{\rho^2} \tag{17}$$

where C is the constant of integration which depends on temperature. The temperature on the inversion curve is clearly not constant. Therefore, we must find the value of C at each point on the inversion curve. To do so, we may use the following thermodynamic relation,

$$H = U + K_{\mathrm{in}} + pv \tag{18}$$

where H, U, and K_{in} are the enthalpy and the potential and kinetic energies of the fluid, respectively. Since H is constant in the Joule–Thomson experiment, then

$$dU + dK_{\mathrm{in}} + d(p/\rho) = 0 \tag{19}$$

If we take the partial derivative of Eq. (19) with respect to ρ at constant temperature, and assume that the change in kinetic energy depends only on temperature, Eq. (19) will be given as

$$(\partial U/\partial \rho)_T = p/\rho^2 - (\partial p/\partial \rho)_T/\rho \tag{20}$$

From comparison of Eq. (20) with Eq. (17) we find C as

$$-\mathrm{C} = \rho(\partial p/\partial \rho)_T = B_T \tag{21}$$

where B_T is the bulk modulus. Therefore, we may write Eq. (17) as

$$\xi = (\partial U/\partial \rho)_T = \frac{(p - B_T)}{\rho^2} \tag{22}$$

4. EXPERIMENTAL TEST

The values of ξ that are obtained for Ar [4] at various densities from Eq. (22) are shown in Fig. 1. $(\partial U/\partial \rho)$ or $(\partial U/\partial r)$, for the effective pair potential, may be compared with the experimental value given for the pair potential. These quantities are not exactly the same but are similar. We have plotted $(\partial U^*/\partial x)$, where $U^* = U/\varepsilon$ and $x = r/r_{\mathrm{m}}$, versus x for argon in Fig. 2 and compared the values with those of the Aziz potential function [5]. As shown in Fig. 2, our first claim is that the points on the inversion curve correspond only to the attractive branch of the effective pair potential [note that for all experimental points, $[(\partial^2 U/\partial x^2) < 0]$. It is interesting to note that the density of the most dense part of the inversion curve, which corresponds to the liquid state, is lower than the density at the minimum of the potential function. This density occurs at the common compression factor point, which is higher than the liquid density [6]. Therefore, the conclusion based on Fig. 2, that all inversion points belong to the

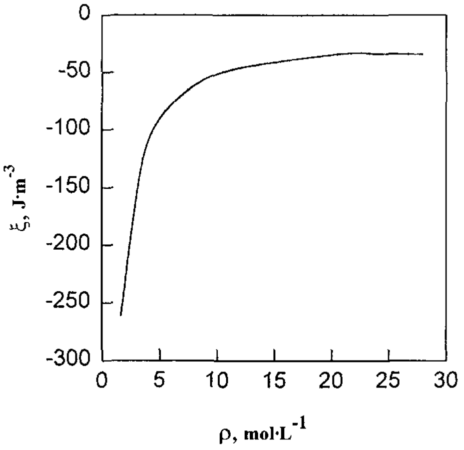

Fig. 1. The slope of the effective pair potential, ξ, as a function of density, for Ar obtained from Eq. (22) on the inversion curve.

attractive branch, is reasonable. So, it is obvious that the density of the inversion curve is lower than the density of the repulsive branch (high density).

The second fact that we would like to explain is the difference between the pair and the effective pair potentials. We may conclude from Fig. 2,

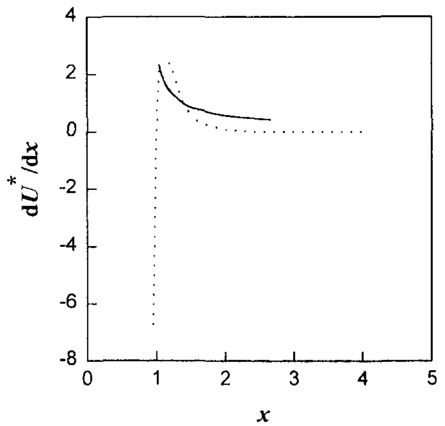

Fig. 2. The slope of the potential function, (dU^*/dx), versus the reduced separation, $x = r/r_m$, obtained from the Aziz potential [5] (dotted curve) and the inversion curve (solid curve).

when the mean molecular separation is between 1.5 and 3 times r_m, that the effective pair potential is lower than the pair potential. This difference is due to the fact that the attraction has a longer range than the repulsion, and we may expect that the contribution of the attraction term in the effective pair potential is more important than its repulsive part. Therefore, we may expect that (dU^*/dx) approaches zero more slowly than that of the pair potential. When the system becomes more dense, i.e., at short separations, the effective pair potential is at a higher energy than the pair potential. This behavior at such short distances is reasonable, because of the importance of the repulsive term of the potential for dense systems. Because of the longer range of attraction compared to repulsion, we may expect that the r_m of the effective pair potential will be less than that of the pair potential. This investigation has also been done for N_2, and the same conclusions were obtained.

5. CONCLUSION

In spite of the previous suggestion [7] that the upper branch of the inversion curve is a good representation of the repulsive part of the pair potential, all points on the inversion curve represent the attractive branch of the effective pair potential (see Fig. 2). The most dense part of the inversion curve corresponds to liquid states, and its density everywhere is lower than the density at the minimum of the effective pair potential. The density corresponds to r_m of the effective pair potential is found to be about 44 $\text{mol} \cdot \text{L}^{-1}$ for Ar [6]. The density at all inversion points is less than 44 $\text{mol} \cdot \text{L}^{-1}$ and, therefore, does not provide any information about the repulsive part of the potential.

Also, using the exact thermodynamic relations, the Joule coefficient, μ_J, can be written as

$$\mu_J = (\partial T/\partial v)_E = -\frac{1}{C_v}(\partial E/\partial v)_T = -\frac{RT^2\rho}{C_v}(\partial Z/\partial T)_\rho \qquad (23)$$

Assuming $(\partial E/\partial v)_T = dU/dv$, then for the state at which $\mu_J = 0$, we get $dU/dr = 0$, which corresponds to the minimum of the effective pair potential, r_m. According to Eq. (23), if there is a single common compression point for a fluid [at which $(\partial Z/\partial T)_\rho = 0$], it is expected to have a single value of r_m for the potential of that fluid for all temperatures. Such a common point may exist only at low temperatures [8]. Therefore, we may conclude that the effective pair potential of a fluid depends on the temperature as well as the density, unlike the isolated pair potential. However, due to the fact that the density on the inversion curve is related to the temperature, it has been possible to express the effective pair potential only in terms of density in this work, in which the result is based on the inversion curve.

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