Comment on
‘Near critical phase behaviour of dilute mixtures’

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The recently published (Gude, M. T., and Teja, A. S., 1994, Molec. Phys., 81, 599) expression for \((\partial P/\partial x_2)_{\rho, T}\) is demonstrated to be valid only at the solvent critical point, and the more general microscopic connection is shown between the isothermal-isobaric finite pressure change \((\partial P/\partial x_2)_{\rho, T}\) and the rearrangement of the solvent structure around an infinitely dilute solute. Finally, there is discussion of some properties of this derivative and some theoretical implications in the interpretation of solvation at near critical conditions.

1. Introduction

The thermodynamic behaviour of dilute near-critical systems depends on microscopic phenomena involving two different length scales, namely, those related to the short ranged (finite) density perturbation induced by the presence of the solute, and to the long ranged (diverging) propagation of this density perturbation to a distance given by the solvent’s correlation length. Even though the coexistence of these two effects makes dilute near-critical mixtures extremely challenging for macroscopic modelling, it provides a useful way to characterize their thermophysical properties into solute induced and compressibility driven contributions [1, 2]. The characterization of these systems for modelling purposes usually takes the form of asymptotic expressions for the mixture’s Helmholtz free energy and its temperature, volume, and composition derivatives around the solvent’s critical point. The usefulness of the resulting asymptotic expressions resides in their mathematical simplicity: they require only the pure solvent thermophysical properties and the critical value of the derivative \((\partial P/\partial x_2)_{\rho, T}\), Krivevskii’s parameter, [3] where \(P\) is the total pressure, \(x_2\) is the mole fraction of solute, \(T\) is the absolute temperature, and \(\rho\) is the solvent’s number density. Typical examples of this asymptotic expressions are given in the literature for the \(K\) distribution factor [4], Henry’s constant [4, 5], solute solubility enhancement [6], and the critical line [7].

The key to success in the modelling of dilute near-critical mixtures is the microscopic understanding of the solvation phenomena, and an appropriate starting point for gaining such an understanding is the microscopic interpretation of the difference of residual chemical potentials between the solute and the solvent, and the related quantities such as \((\partial P/\partial x_2)_{\rho, T}\) around and away from the solvent’s critical point [1, 2]. In a recently published paper on the near-critical behaviour of dilute
mixtures, Gude and Teja [8] presented the following expression (their equation (6)):

$$
\left( \frac{\partial P}{\partial x_2} \right)_{T, \rho}^\infty = \rho k T (1 - C_{12}^n),
$$

(1)

which was suggested as a statistical mechanical interpretation of $(\partial P/\partial x_2)_{\rho,T}^n$, i.e. [1–3, 9, 10],

$$
\left( \frac{\partial P}{\partial x_2} \right)_{T, \rho}^\infty = \frac{\rho \tilde{v}_2^\infty - 1}{\kappa} = \rho k T (C_{11}^n - C_{12}^n),
$$

(2)

where $\tilde{v}_2^\infty$ is the solute partial molar volume at infinite dilution, $\kappa$ is the solvent isothermal compressibility, $C_{ij}$ is the direct correlation function integral for the $ij$ pair interactions, and superscripts $n$ and $\infty$ denote pure component and infinite dilution, respectively. As we will demonstrate below, the RHS of equation (1) is not the statistical mechanical expression for the derivative $(\partial P/\partial x_2)_{\rho,T}^n$ but for the related quantity $N(\partial P/\partial N_2)_{\rho,N_1}^{\infty}$, that coincides with $(\partial P/\partial x_2)_{\rho,T}^n$ only at the solvent's critical point, i.e.,

$$
\lim_{T, \rho \to \text{critical}} N \left( \frac{\partial P}{\partial x_2} \right)_{T, \rho, N_1}^{\infty} = \left( \frac{\partial P}{\partial x_2} \right)_{T, \rho}^{\infty}
$$

(3)

since in this limit $C_{11}^n \to 1$.

In this note we first review how the change of Gibbs free energy in the solvation process relates to the $(\partial P/\partial x_2)_{\rho,T}^n$, and how this derivative represents the amplitude of the finite structural perturbation of the solvent around the solute. Then, we derive the thermodynamic and statistical mechanical relations between the right hand sides of equations (1) and (2). Finally, we discuss some additional properties of $(\partial P/\partial x_2)_{\rho,T}^n$ associated with the behaviour of the microstructure of these systems.

2. Background

Let us consider a system of $N$ solvent molecules in a volume $V$, at constant temperature $T$, and total pressure $P$. From a residual properties viewpoint this system can be thought as an ideal solution of $(N - 1)$ molecules labelled solvent and one molecule labelled solute whose intermolecular potential parameters are all identical the same. Therefore, the formation of an infinitely dilute solution can be portrayed as one in which an original solvent molecule (the solute in the ideal solution) mutates to a final solute molecular by a coupling parameter charging (see reference [11] for details). The isothermal–isobaric coupling work involved in such a (solvation) process is equal to the difference of residual chemical potential between the solute and the solvent at constant temperature and either constant volume or pressure $[1, 2],$

$$
\mu_{2}^{\infty}(T, P) - \mu_{1}^{\infty}(T, \rho) = \mu_{2}^{\infty}(T, \rho) - \mu_{1}^{\infty}(T, \rho)
$$

(4)

$$
\int_{0}^{\rho_{P}} \left( \frac{\partial P}{\partial x_2} \right)_{T, \rho}^\infty \, d\rho.
$$

Equation (4) can also be written in more familiar terms as [12]

$$
\ln [H_2(T, P)/f_2^{\infty}(T, P)] = \beta \int_{0}^{\rho_{P}} \left( \frac{\partial P}{\partial x_2} \right)_{T, \rho}^\infty \, d\rho,
$$

(5)
where $H_2$ and $f^*_l$ are Henry's constant of the solute and the fugacity of the pure solvent, respectively. Equations (4) and (5) indicate that, from a macroscopic viewpoint, $(\partial P/\partial x_2)^{\infty}_{T,\rho}$ measures the isothermal density dependence of the change of Gibbs free energy in the formation of an infinitely dilute solution, or alternatively, the isothermal density dependence of the ratio of solute to solvent fugacity coefficients.

To focus on the significance of such a connection we now make the microscopic interpretation of $(\partial P/\partial x_2)^{\infty}_{T,\rho}$ by invoking the Kirkwood–Buff fluctuation formalism of mixtures in its two versions, i.e., in terms of total correlation function integrals (TCFIs) [13], and direct correlation function integrals (DCFIs) [14]. The derivative $(\partial P/\partial x_2)^{\infty}_{T,\rho}$ can be written in terms of TCFIs as [1]

$$
\left( \frac{\partial P}{\partial x_2} \right)^{\infty}_{T,\rho} = \frac{\rho^2 kT(G_{11}^1 - G_{12}^1)}{1 + \rho G_{11}^0},
$$

(6)

where the TCFIs are given by [13]

$$
G_{ij} = \int h_{ij} \, dr = \hat{h}_{ij}(0)
$$

(7)

with $\hat{h}_{ij}(k)$ the Fourier transform of the total $ij$ pair correlation function, $h_{ij}(r) = [g_{ij}(r) - 1]$, and $g_{ij}(r) = \langle g_{ij}(r, \omega_i, \omega_j) \rangle_{\omega_i, \omega_j}$ the spatial (unweighted angle average) centre-to-centre $ij$ pair distribution function [15]. Alternatively, $(\partial P/\partial x_2)^{\infty}_{T,\rho}$ can be written in terms of DCFIs as [2, 9]

$$
\left( \frac{\partial P}{\partial x_2} \right)^{\infty}_{T,\rho} = \rho kT(C_{11}^1 - C_{12}^1),
$$

(8)

where the DCFIs are defined as [14]

$$
C_{ij} = \rho \int c_{ij} \, dr = \rho \hat{c}_{ij}(0),
$$

(9)

and $\hat{c}_{ij}(k)$ is the Fourier transform of the direct $ij$ pair correlation function. Equations (6) and (8) indicate that, from a microscopic viewpoint, $(\partial P/\partial x_2)^{\infty}_{T,\rho}$ measures the isothermal-isochoric finite pressure change induced by the microscopic rearrangement of the solvent structure around the infinitely dilute solute relative to the solvent structure in the absence of solute. Therefore, that derivative measures macroscopically the amplitude of the solute-induced perturbation of the solvent structure, i.e., a solute-induced effect. This effect propagates out a distance given by the solvent's correlation length $\xi$ and, because $\xi^2$ is proportional to the solvent's isothermal compressibility $\kappa$, the propagation distance diverges at the solvent's critical point even though the amplitude of the solute-induced effect remains finite.

It is important to note that, though exact, equation (8) is somewhat restrictive in that it involves the 'atomic' Ornstein–Zernike equation [16]. In contrast, equation (6) applies to mixtures involving any type of molecular anisotropy [15]. We must also realize that, even though the system's TCFIs diverge at the solvent's critical
point, i.e., $G_{12}^0 \sim \xi^2 \sim \kappa$, their ratios remain finite [1]. In particular, at the solvent's critical point, equations (6) and (8) define Krchkevski's parameter, i.e.,

$$
\left( \frac{\partial P}{\partial X_2} \right)_{T_2,\rho_2} = \rho_c kT_c \left( 1 - \frac{G_{12}^0}{G_{11}^0} \right)
$$

where $F[\ldots]$ denotes 'function of', and 'SR' indicates the short-ranged contribution to the TCFIs, and

$$
\left( \frac{\partial P}{\partial X_2} \right)_{T_2,\rho_2} = \rho_c kT_c [1 - C_{12}^\infty],
$$

because $(C_1^1)_{T_2,\rho_2} = 1$ [3]. Note that for systems composed of spherically symmetric molecules the ratio $(G_{12}^0/G_{11}^0)_{T_2,\rho_2}$ in equation (10) reduces to $(C_1^1)_{T_2,\rho_2}$ after invoking the 'atomic' OZ equation [9]. In summary, because the critical values of the ratio of solute–solvent to solvent–solvent DCFI's and TCFI's are finite, Krchkevski's parameter is always finite, a conclusion already reached by Levelt Sengers on purely thermodynamic grounds [6].

3. Derivation of equation (2)

Let us take the total volume of the binary system as a function of the pressure $P$, the temperature $T$, and the number of molecules of solvent and solute $N_1$ and $N_2$, i.e., $V = V(T, P, N_1, N_2)$. Now, by invoking the chain rule for the derivatives, we have that,

$$
\left( \frac{\partial V}{\partial N_2} \right)_{T,\rho} \cdot \left( \frac{\partial N_2}{\partial P} \right)_{T,V,N_1} \cdot \left( \frac{\partial P}{\partial V} \right)_{T,N_1} = -1
$$

and, after recalling the definition of partial molar volume $\bar{v}_1$ and isothermal compressibility $\kappa$, equation (12) can be rearranged as

$$
N \left( \frac{\partial P}{\partial N_2} \right)_{T,V,N_1} = \frac{\rho \bar{v}_2}{\kappa}.
$$

Likewise, by taking $v = V/N = v(T, P, x_2)$ the chain rule gives

$$
\left( \frac{\partial P}{\partial x_2} \right)_{T,\rho} = \frac{\rho (\bar{v}_2 - \bar{v}_1)}{\kappa}.
$$

Therefore, equations (13) and (14) are related to each other by

$$
N \left( \frac{\partial P}{\partial N_2} \right)_{T,\rho,N_1} = \left( \frac{\partial P}{\partial x_2} \right)_{T,\rho} + \frac{\rho \bar{v}_1}{\kappa},
$$

which is valid at any solute concentration. At infinite dilution of component 2, equations (13) and (15) reduce to

$$
N \left( \frac{\partial P}{\partial N_2} \right)_{T,V,N_1}^\infty = \frac{\rho \bar{v}_2^\infty}{\kappa}.
$$
and [17]
\[
N\left(\frac{\partial P}{\partial N_2}_{T,\rho,N_1}^\infty\right) = \left(\frac{\partial P}{\partial X_2}_{T,\rho}^\infty\right) + \kappa^{-1},
\]
(17)
with
\[
\left(\frac{\partial P}{\partial X_2}_{T,\rho}^\infty\right) = \frac{\rho e^2}{\kappa} - 1,
\]
(18)
which is the first line of equation (2). For more details see appendix A of reference [9]. By invoking once again Kirkwood–Buff formalism in terms of DCFIs, the RHS of equation (16) becomes [9, 18, 19]
\[
\frac{\rho e^2}{\kappa} = \rho k T(1 - C_{12}^\infty),
\]
(19)
where [14]
\[
\kappa^{-1} = \rho k T(1 - C_{11}^\infty).
\]
(20)
Finally, from equations (16–20) we obtain
\[
\left(\frac{\partial P}{\partial X_2}_{T,\rho}^\infty\right) = \rho k T(1 - C_{12}^\infty) - \kappa^{-1}
\]
\[
= \rho k T(C_{11}^\infty - C_{12}^\infty),
\]
(21)
which is the second line of equation (2). Therefore, according to equations (13–21) Gude and Teja’s equation (6) is not the general statistical mechanical expression for the derivative \(\partial P/\partial X_2\)_{T,\rho}, but for the derivative \(N(\partial P/\partial N_2)_{T,\rho,N_1}\). These two derivatives become identical only at the solvent critical point, i.e.,
\[
\lim_{\rho, T \to \text{critical}} \kappa^{-1} = 0 \Rightarrow (C_{11}^\infty)_{\rho,T_c} = 1
\]
(22)
and
\[
\lim_{T,\rho \to \text{critical}} N\left(\frac{\partial P}{\partial N_2}_{T,\rho,N_1}^\infty\right) = \left(\frac{\partial P}{\partial X_2}_{T,\rho}^\infty\right)
\]
\[
= \rho_e k T(1 - C_{12}^\infty)_{\rho,T_c}.
\]
(23)

4. Discussion

In this note we have analysed the microscopic expressions for the derivative \(\partial P/\partial X_2\)_{T,\rho} in terms of DCFIs and TCFIs by invoking the Kirkwood–Buff fluctuation formalism of mixtures. This derivative can be rigorously interpreted also by defining the more intuitive statistical mechanical quantity \(N_{ex}^\infty\),
\[
N_{ex}^\infty = \rho(G_{12}^\infty - G_{11}^\infty),
\]
(24)
which represents the excess number of solvent molecules around the infinitely dilute solute relative to that number around any solvent molecule (the ideal solution). From equations (6) and (24) we then obtain [1]:
\[
N_{ex}^\infty = -\kappa\left(\frac{\partial P}{\partial X_2}_{T,\rho}^\infty\right).
\]
(25)
To gain some additional insight into the connection between the structural perturbation of the solvent, the size of the derivative \( (\partial P/\partial x_2)_{T,\rho}^\infty \), the quantity \( N_{st}^\infty \), and the solute induced effect we invoke the following rigorous expression for the solute partial molar volume at infinite dilution [1]:

\[
\bar{v}_2^\infty = \rho^{-1} \left[ 1 + \kappa \left( \frac{\partial P}{\partial x_2} \right)_{T,\rho}^\infty \right].
\]  

Therefore, from equations (25) and (26) it follows that

\[
N_{st}^\infty = 1 - \rho \bar{v}_2^\infty.
\]  

Alternatively, by invoking the unambiguous separation between the solvation and compressibility driven contributions to the solute partial molar volume at infinite dilution, \( \bar{v}_2^\infty \)(SR) and \( \bar{v}_2^\infty \)(LR), respectively [1, 2], i.e.,

\[
\bar{v}_2^\infty = \rho^{-1} + \rho^{-1} \kappa^\text{IG} \left( \frac{\partial P}{\partial x_2} \right)_{T,\rho}^\infty + \rho^{-1} \kappa' \left( \frac{\partial P}{\partial x_2} \right)_{T,\rho}^\infty,
\]  

Equation (27) can be recast as

\[
N_{st}^\infty = -\kappa^\text{IG} \left( \frac{\partial P}{\partial x_2} \right)_{T,\rho}^\infty - \kappa' \left( \frac{\partial P}{\partial x_2} \right)_{T,\rho}^\infty,
\]  

where \( \kappa' = \kappa - \kappa^\text{IG} \) and \( \kappa^\text{IG} = \beta/\rho \) are the residual and ideal gas compressibilities, respectively. Equation (29) indicates that the total excess number of solvent molecules around the solute is made up of the finite contribution resulting from the short-range (SR) solvent’s density perturbation around the solute (solvation), and the diverging contribution resulting from the long-range (LR, compressibility driven) propagation of the density perturbation.

Therefore, from equations (28) and (29) the short- and long-range contributions to \( N_{st}^\infty \) are connected to the corresponding contributions to the solute partial molar volume at infinite dilution by

\[
N_{st}^\infty \text{(SR)} = 1 - \rho \bar{v}_2^\infty \text{(SR)}
\]  

and,

\[
N_{st}^\infty \text{(LR)} = -\rho \bar{v}_2^\infty \text{(LR)}.
\]  

Thus, equation (30) provides another microscopic interpretation of \( (\partial P/\partial x_2)_{T,\rho}^\infty \) as

\[
\left( \frac{\partial P}{\partial x_2} \right)_{T,\rho}^\infty = -\rho kTN_{st}^\infty \text{(SR)}
\]  

and well as for Krichelukii’s parameter

\[
\left( \frac{\partial P}{\partial x_2} \right)_{T,\rho}^\infty = -\rho_c kTN_{st}^\infty \text{(SR)}.
\]
Finally, after recalling the definition of the volumetric solute-induced effect, we can recast equations (32) and (33) as

$$\left( \frac{\partial P}{\partial X_2} \right)_{\tau, \rho} = \rho^2 k T (\bar{v}_2^e (\text{SR}) - \rho^{-1})$$

(34)

and

$$\left( \frac{\partial P}{\partial X_2} \right)_{\tau, \rho} = \rho^2 k T (\bar{v}_2^e (\text{SR}) - \rho^{-1})$$

(35)

In summary, the derivative $(\partial P/\partial X_2)_{\tau, \rho}$ can be written as equations (6), (8), (32), and (34) whose corresponding expressions for Krizevskii's parameter are equations (10), (11), (33), and (35). All these expressions indicate that $(\partial P/\partial X_2)_{\tau, \rho}$ measures the (finite) microscopic rearrangement of the solvent structure around the infinitely dilute solute relative to the solvent structure (ideal solution), and therefore that the solvation phenomenon is driven not by the strength of the solute–solute interactions (represented by $C_{12}^e$ or $G_{12}^e$), as frequently suggested [8, 17], but by the difference in strength between the solute–solvent and the solvent–solvent interactions (represented by $(C_{12}^e - C_{11}^e)$ or $(G_{12}^e - G_{11}^e)$), i.e., by the solute–solvent intermolecular asymmetry. In fact, if the strength of the solute–solvent interactions is the same as for the solvent–solvent interactions, the system will behave as an ideal solution regardless of how strong those interactions might be. In such a case the solute behaves as a solvent molecule, i.e., the solvent microstructure is not disturbed by the solute so that $G_{12}^e = G_{11}^e$, $(\partial P/\partial X_2)_{\tau, \rho} = 0$ and, consequently, the change of Gibbs free energy (equation (4)) is zero.

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References