On the Properties of Equations of State at Infinite Pressure

Stefano Brandani
Institute of Materials and Processes, School of Engineering and Electronics, University of Edinburgh, Sanderson Building, The King's Buildings, Edinburgh EH9 3JL, United Kingdom

Vincenzo Brandani
Dipartimento di Chimica, Ingegneria Chimica e Materiali, Universita' de L'Aquila, Monteluco di Roio, I-67040 L'Aquila, Italy

DOI 10.1002/aic.11114
Published online February 14, 2007 in Wiley InterScience (www.interscience.wiley.com).

Using the exact solution valid for hard spheres in the proximity of infinite pressure, the correct limits for the compressibility (infinite), the residual Helmholtz energy (infinite), and the excess Helmholtz energy (finite) are derived. All the equations of state commonly used in chemical engineering applications fail to fulfil one of these limits, and are shown to be inconsistent in the limit of infinite pressure. *AIChE J*, 53: 986–988, 2007
Keywords: themodynamics/classical, phase equilibrium, equations of state, infinite pressure, Helmholtz energy

Introduction

An equation of state can be expressed in general as a function of the different contributions that characterize the departure from ideality

$$z = 1 + z^{rep} + z^{attr} \tag{1}$$

As the pressure increases and tends to infinity, the dominant contribution becomes that of the repulsive forces, since these tend to infinity, and all the other terms remain finite. Therefore, to determine the correct behavior in this limit all the finite contributions may be neglected, that is

$$z_\infty \approx 1 + z^{rep} \tag{2}$$

From this approximation, it is possible to derive the reduced Helmholtz energy

$$\widetilde{A}_\infty = \frac{A_\infty(T,\rho) - A_\infty^{IG}(T,\rho)}{RT} = \int_0^\rho \frac{z^{rep}}{\rho} d\rho \tag{3}$$

and the residual reduced Helmholtz energy

$$\widetilde{A}_\infty^{res} = \frac{A_\infty(T,P) - A_\infty^{IG}(T,P)}{RT} = \widetilde{A}_\infty - \ln(z_\infty) \tag{4}$$

While it is commonly accepted that the compressibility should be infinite at infinite pressure, it is not obvious what should be the correct limit for the residual Helmholtz energy, and also what will be the resultant reduced excess Helmholtz energy, which can be obtained from

$$\widetilde{A}_\infty^{EX} = \sum w_i\left(\widetilde{A}_{\infty M} - \widetilde{A}_{\infty i}\right) + \sum w_i \ln\left(\frac{z_{\infty i}}{z_{\infty M}}\right) \tag{5}$$

where w_i is the mole fraction of component i in the mixture.

Brandani and Brandani[1] showed that the residual Helmholtz energy tends to infinity as the high pressure limit is approached, comparing the predictions of simple equations of state,

Correspondence concerning this article should be addressed to S. Brandani at s.brandani@ed.ac.uk.

and the high-pressure data for water (Saul and Wagner[2]). Brandani et al.[3] showed that for all common expressions of the repulsive term of the form

$$z^{rep} = \frac{f(\zeta)}{(1-\zeta)^m}, \tag{6}$$

where ζ is the reduced density, and $f(\zeta)$ is a function that is finite at infinite pressure, the correct limit is obtained for the compressibility, but the residual Helmholtz energy tends to infinity only for $m > 1$. They concluded that all cubic EOS, which are characterized by the exponent $m = 1$, are thermodynamically inconsistent at infinite pressure.

Brandani et al.[3] also showed that excess Helmholtz energy is infinite at infinite pressure, unless the following expression is used to define the size parameter of the equation of state

$$b_M^{(m-1)/m} = \sum w_i b_i^{(m-1)/m}. \tag{7}$$

One can observe that Eq. 7 is automatically fulfilled for cubic EOS, which predict a finite excess Helmholtz energy at infinite pressure. For all EOS characterized by $m > 1$ Eq. 7 represents an arbitrary condition on the size parameter which does not have a physical meaning. More importantly, imposing this condition does not yield the thermodynamically correct limit at zero pressure (Wong and Sandler[4]). This led Brandani et al.[3] to conclude that the excess Helmholtz energy was likely to be infinite at infinite pressure.

This contribution aims to identify unambiguously what are the correct limits at high-pressure or high-densities that are valid for the residual and the excess Helmholtz energies.

Theory

Having recognized that in the limit of infinite pressure one has to consider only the repulsive terms of the equation of state, it is possible to reach a general result by limiting the analysis to the exact analytical solution obtained by Tonks[5] for hard spheres. Tonks[5] derived the exact analytical limit by studying the behavior of an isolated vacancy for the one-dimensional (1-D) gas of hard spheres, and extended his treatment to two and three dimensions. He showed that as the close-packed limit is approached the correct expression for the compressibility is of the form

$$z_\infty = \frac{f(\zeta)}{1-\zeta^{1/3}}, \tag{8}$$

Tonks[5] showed that for a cubic lattice $f(\zeta) = 1$, and that this is also the likely solution for all other close-packed limits. We will, therefore, use this condition without loss of generality, since the behavior in the proximity of the limit of infinite pressure is in fact determined by the denominator in Eq. 8 and not the exact finite value of $f(\zeta)$. Therefore

$$\widetilde{A}_\infty = -3\ln\left(1-\zeta^{1/3}\right) = 3\ln\ z_\infty \tag{9}$$

and the residual reduced Helmholtz energy is given by

$$\widetilde{A}^{res}_\infty = \widetilde{A}_\infty - \ln\left(z_\infty\right) = 2\ln\ z_\infty. \tag{10}$$

As would be expected, the exact solution of Tonks[5] yields the correct limits for both the compressibility, and the residual Helmholtz energy which are infinite at infinite pressure. When the result is extend to the reduced excess Helmholtz energy, one obtains

$$\widetilde{A}^{EX}_\infty = 2\sum w_i \ln\left(\frac{z_{\infty M}}{z_{\infty i}}\right) = \sum w_i \ln\left(\frac{b_M}{b_i}\right)^2 \tag{11}$$

Therefore, in the limit as pressure goes to infinity the excess Helmholtz energy is finite, regardless of the mixing rule used for the size parameter.

From this analysis it is possible to state that at infinite pressure a thermodynamically consistent equation of state must have

(1) an infinite compressibility;
(2) an infinite residual Helmholtz energy;
(3) a finite excess Helmholtz energy.

Conclusions

Using the analytical expression of Tonks[5], valid in the limit of infinite pressure, it is possible to define the requirements for thermodynamic consistency of any equation of state: the residual Helmholtz energy should be infinite, while the excess Helmholtz energy should be finite at infinite pressure.

Since cubic equations of state yield a finite residual Helmholtz energy and all the noncubic equations of state in common use yield an infinite excess Helmholtz energy, we are able to conclude that we are not aware of any equation of state that is thermodynamically consistent at infinite pressure.

This result has an important consequence on mixing rules based on the infinite pressure limit (Wong and Sandler[4]). We can now state that the Wong-Sandler mixing rules are theoretically correct, and that they are not applicable to noncubic equations of state due to the thermodynamic inconsistency identified in this article.

Acknowledgment

The support of the Royal Society Wolfson Research Merit Award is gratefully acknowledged.

Notation

$\tilde{A}$ = reduced Helmholtz energy
b = volume parameter or covolume of the EOS, m^3/mol
w_i = mole fraction of component i
z = compressibility

Greek letters

ρ = density, mol/m^3
ζ = reduced density (1 at infinite pressure)

Superscripts and subscripts

∞ = in the proximity of the limit as pressure goes to infinity
attr = attractive term

EX = excess
i = component i
M = mixture
rep = repulsive term
res = residual

Literature Cited

1. Brandani S, Brandani V. On the inapplicability of mixing rules based on the infinite pressure reference state. *Fluid Phase Equilibria.* 1996;121: 179–184.
2. Saul A, Wagner W. A Fundamental equation for water covering the range from the melting line to 1273 k and pressures up to 25000 Mpa. *J Phys Chem Ref Data*. 1989;18:1537–1564.
3. Brandani F, Brandani S, Brandani V. The Wong-Sandler mixing rules and EOS which are thermodynamically consistent at infinite pressure. *Chem Eng Sci*. 1998;53:853–856.
4. Wong DSH, Sandler SI. A Theoretically correct mixing rule for cubic equations of state. *AIChE J*. 1992;38:617–680.
5. Tonks L. The complete equation of state of one, two and three-dimensional gases of hard elastic spheres. *Phys Rev*. 1936;50:955–963.

Manuscript received Nov. 8, 2006.