New Methods for Locating Phase Boundaries

G. Fescos, J. M. Kincaid, and G. Morrison

A new geometric representation for the dew/bubble conditions of a special class of polydisperse fluids is used to develop series expansion representations for the location of the top of the dew/bubble and shadow curves and for an expansion around the top of the dew/bubble and shadow curves. An excellent approximation for the one-component van der Waals coexistence is given as a special illustration of the method.

KEY WORDS: coexistence curve; critical point; dew/bubble curve; phase transitions; polydisperse.

1. INTRODUCTION

In a recent study of a special class of polydisperse fluids we found a particularly simple geometric representation of the dew/bubble conditions [1]. In that representation the problem of locating the dew/bubble and shadow curves is reduced to locating the points of intersection of two curves. Once these points of intersection are located, the composition of the nucleating phase is easily determined. In this paper we show that it is possible to obtain explicit solutions of the dew/bubble conditions in the form of power series expansions. By forming Padé approximants from these series it is possible to create compact expressions for the phase boundaries that provide very accurate representations over a wide range of temperatures and densities. Although the models on which we demonstrate our techni-
que are rather simple, it seems likely that the method may be applied to more complicated models.

We begin in Section 2 by describing our method for the simple case of the one-component van der Waals model. In Section 3 we define two models for polydisperse fluids for which we exhibit explicit solutions and express the dew/bubble conditions in a form appropriate for our calculations. Section 4 contains a description of our series expansion method for locating the top of the dew/bubble and shadow curves and for an expansion around the top of the dew/bubble curve.

2. THE ONE-COMPONENT VAN DER WAALS MODEL

The van der Waals model provides one of the simplest models of a fluid that exhibits the qualitative features of most real fluids. Although the coexistence curve of the van der Waals model is discussed in almost every textbook on thermodynamics, no closed-form expression has been found to represent its coexistence curve. In this section we come very close to providing such an expression.

Let us begin by stating the relevant equations for the pressure, \( p \), and chemical potential, \( \mu \), of the model:

\[
p(T, \rho) = \frac{8T\rho}{(3 - \rho)} - 3\rho^2
\]  

and

\[
\mu(T, \rho) = \left[ \ln \left( \frac{\rho}{(3 - \rho)} \right) + \frac{\rho}{(3 - \rho)} \right] - \frac{9}{4}\rho
\]

Here \( \rho \) is the number density and \( T \) is the temperature. [We have used dimensionless variables: energies are reduced by \( 8a/(27b) \), volumes by \( 3b \), and pressures by \( a/(27b^2) \), where \( a \) and \( b \) are the van der Waals constants.] Two phases with densities denoted by \( x \) and \( y \), respectively, coexist in equilibrium if

\[
p(T, x) = p(T, y) \quad \text{and} \quad \mu(T, x) = \mu(T, y)
\]

For \( T > 1 \) the only solution of these equations is the trivial solution \( x = y \) —there is only one phase. When \( T < 1 \), the nontrivial solutions of these two equations, \( x(T) \) and \( y(T) \), define the coexistence curve. In addition to the usual geometric representations for the equilibrium conditions [e.g., the equal area rule, the bitangent construction, or the minimization of \( \mu(T, p) \)], we find it useful (especially in the case of the polydisperse fluid