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# Molecular-level simulation of bubble and dew points of fluid mixtures and application to refrigerant cycle design☆

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ABSTRACT

Molecular simulation is an increasingly important and useful tool in the design of devices based on many types of chemical phenomena. Such methods for the simulation of all types of vapour–liquid equilibrium (VLE) are particularly important, because they potentially permit their direct application to the design of refrigeration processes. Several molecular simulation methods exist for the calculation of VLE in the cases of flash calculations and bubble-point calculations for fluid mixtures. However, implementations for other VLE problems such as dew-points remain challenging. We present an algorithm for the calculation of all four types of these VLE phenomena in binary mixtures. We illustrate it for a 30 mass% R32/R134a binary refrigerant mixture by means of example dew- and bubble-point problems, in addition to the calculation of $P-h$ and $T-h$ diagrams. We also demonstrate its application to the simulation of a vapour compression refrigeration cycle involving the refrigerant mixture.



# Simulation au niveau moléculaire des points d'ébullition et de rosée de mélanges de fluides et application à la conception des cycles frigorifiques

*Mots clés :* Réfrigération ; Simulation moléculaire ; R32 ; R134a ; Points de rosée ; Points d'ébullition

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**Nomenclature**

| | |
|---|---|
| $c$ | Number of system components |
| $D$ | dipole moment vector |
| COP | Coefficient of Performance |
| $h$ | molar enthalpy |
| $H$ | total enthalpy |
| $k$ | Boltzman's constant |
| $L$ | distance between LJ sites on molecule |
| LJ | Lennard-Jones potential |
| $n$ | iteration counter |
| $N$ | number of particles |
| $P$ | pressure |
| $P^*$ | pure-component vapour pressure |
| PE | pseudo ensemble |
| GEMC | Gibbs Ensemble Monte Carlo method |
| $r$ | residual quantity (in excess of ideal gas value) |
| $r$ | distance between molecular LJ sites |
| RGEMC | Reaction Gibbs Ensemble Monte Carlo method |
| $T$ | temperature |
| $u$ | intermolecular potential function |
| $U$ | configurational energy |
| $V$ | volume |
| VCRC | vapour compression refrigeration cycle |
| VLE | vapour–liquid equilibrium |
| $w$ | overall vapour–liquid mole fraction |
| $x$ | liquid mole fraction |
| $y$ | vapour mole fraction |
| $Y$ | $P$ or $T$ in a dew point or bubble point calculation |
| $z$ | mole fraction |
| $\rho$ | density |
| $\sigma$ | on the vapour–liquid coexistence curve |
| $\omega$ | molecular orientation vector |

## 1. Introduction

Advances in computer technology have enabled molecular-level simulation methodology to become a useful tool applicable to many engineering problems involving fluids (*e.g.*, Ungerer et al., 2007; Maginn, 2009; Maginn and Elliott, 2010; Theodorou, 2010; Meunier et al., 2011). We focus here on molecular simulation methods based on classical statistical mechanics, whose sole input requirement is a description of the interactions (force fields) between the molecules of the system (Allen and Tildesley, 1997; Frenkel and Smit, 2002). A significant advantage of the approach is that, once a force field for a given system is available, it can be used to predict many different system thermodynamic and transport properties, unlike the semi-empirical macroscopic approach, which typically requires different equations for different properties and corresponding data to fit the parameters. Due to its fundamental nature, it can also be used to predict properties beyond the range of applicability of the empirical equations. Molecular simulation can potentially supplement or replace the semi-empirical approach when experimental measurements are unavailable, inaccurate, or expensive to obtain.

In the refrigeration and other industries, such methods can provide a molecular understanding and predictive capability for processes underlying phase equilibria. Thermodynamic property prediction for refrigerants is traditionally carried out by means of empirical equations fitted to sets of experimental data. Such equations for many refrigerants have been incorporated in the software program REFPROP (Lemmon et al., 2013), which employ multi-parameter volumetric equations of state involving the order of 40 parameters and additional equations for thermal properties for each fluid, together fitted to thousands of experimental data points. Volumetric properties can also be obtained using well-known cubic equations of state, which incorporate a much smaller number of parameters (fewer than 10), but the results are not generally of quantitative accuracy (*e.g.*, Valderrama, 2003; Polishuk, 2011). The extension to mixtures of both these macroscopic approaches requires the use of empirical rules to calculate the mixture cross-species parameters, which can lead to a decline in accuracy. In contrast to the macroscopic approaches, force fields needed for the implementation of molecular simulation methodology typically require a relatively small number of parameters (fewer than 10), and the results for many properties are of quantitative accuracy.

Force fields have become available in recent years for many fluids, particularly those relevant to the petrochemical industry (Ungerer et al., 2005). Although ideal gas thermodynamic property prediction, which is required for thermal properties, is well in hand, progress in first-principles force field development for calculation of the residual thermodynamic properties of complex fluids such as those that arise in refrigeration is still in its infancy, and the vast bulk of force fields available in the literature have been determined by fitting the parameters in the force field model equations to vapour–liquid equilibrium (VLE) data for pure fluids. Mixture force fields are obtained by various methods based on the pure fluid force fields. However, it has recently been shown that it is possible to develop force fields for complex fluids such as fluoropropene-based refrigerants using a minimum of experimental data (Raabe and Maginn, 2010).

In addition to force fields for refrigerant working fluids, molecular-based computational algorithms for the relevant properties and processes involved are required. Several groups have developed methods for the prediction of Joule–Thomson inversion curves, which depend only on volumetric properties (*e.g.*, Colina and Müller, 1997). Thermally related properties such as heat capacity, iso-enthalps, iso-entropes and Joule–-Thomson coefficients present a more significant challenge, and their study by molecular simulation approaches has been relatively rare. Ungerer et al. (1999, 2007) devised a method to calculate heat capacities. A general algorithm to simulate systems at specified total internal energy or enthalpy (Smith and Lísal, 2002) has been used to predict pressure-enthalpy diagrams, iso-enthalps and Joule–Thomson coefficients for the refrigerant R32 (Lísal et al., 2003). An algorithm to simulate systems at specified total entropy (Smith et al., 2006) has been combined with several existing approaches for other processes to simulate all stages of a vapour compression refrigeration cycle (VCRC), and applied to the pure fluid refrigerants R125 and R134a (Figueroa-Gerstenmaier et al., 2007).