Probing free jet expansions of supercritical fluids

This article has been downloaded from IOPscience. Please scroll down to see the full text article.
2009 Phys. Scr. 80 048127
(http://iopscience.iop.org/1402-4896/80/4/048127)

View the table of contents for this issue, or go to the journal homepage for more

Download details:
IP Address: 141.20.76.101
The article was downloaded on 22/07/2010 at 07:49

Please note that terms and conditions apply.
Probing free jet expansions of supercritical fluids

W Christen and K Rademann

Institut für Chemie, Humboldt-Universität zu Berlin, Brook-Taylor-Strasse 2, 12489 Berlin, Germany
E-mail: christen@wolfgang-christen.net

Received 21 February 2009
Accepted for publication 28 August 2009
Published 1 October 2009
Online at stacks.iop.org/PhysScr/80/048127

Abstract

Attempting to improve the comprehension of supersonic molecular beams at elevated pressures we present a comparative study of thermodynamic descriptions of the terminal flow velocity in free jet expansions. As model system we choose carbon dioxide due to its widespread utilization in supercritical fluid technology. Numerical results for the thermodynamic quantities are obtained using a high accuracy equation of state explicit in the Helmholtz free energy. The influence of pressure and temperature on the beam velocity is investigated for a broad range of stagnation conditions. A consistent physical picture is obtained for calculations employing the initial and final molar enthalpies, while enormous discrepancies are found for descriptions based on the molar isobaric heat capacity or the heat capacity ratio. The deviations are particularly pronounced at the gas–liquid phase transition and in the vicinity of the critical point and can be related to the diverse assumptions of ideal gas behavior. It is shown that computations using real fluid enthalpies permit to assess the fraction of condensation in supersonic jets.

PACS numbers: 34.10.+x, 37.20.+j, 51.30.+i, 47.40.Ki, 82.60.Fa

(Some figures in this article are in colour only in the electronic version.)

1. Introduction

Supersonic molecular beams constitute a notably versatile method in modern physical chemistry [1–3]. They are of prime importance in research areas such as analytical chemistry, cluster science, heterogeneous catalysis, optical spectroscopy, quantum physics, surface science and thin film growth. Accordingly, the main attention is on the numerous applications provided by supersonic jets. In contrast, more fundamental aspects such as the evolution of beam properties with stagnation pressure have not been investigated in great detail. Until now, only the isentropic expansion of ideal gases into vacuum may be modeled readily [4]. Molecular beams of real gases such as carbon dioxide or ethylene present a significantly more complicated and virtually unexplored situation, particularly at higher stagnation pressures. Elevated pressures, however, are required for the growth of weakly bound molecular clusters. Increased stagnation pressures are also encountered in supersonic jet expansions of supercritical fluids. These have evolved as an alternative to conventional organic solvents and are frequently employed in analytical applications. Molecular beams from supercritical solutions [5] permit the fabrication of nanoparticles [6, 7] of non-volatile, poorly soluble, or thermally labile compounds, and the transfer of such substances into the gas phase. The latter possibility is particularly attractive for pharmaceutical and biomedical applications [8, 9]. Despite the promising prospects of beams from supercritical fluids, only a few basic studies of high pressure jets have been performed. In these cases, however, exciting new features have been reported for supersonic beams of He [10–12], H₂ [13], and CO₂ [14, 15] at conditions far from the ideal gas behavior. Hence, very essential questions such as the influence of stagnation pressure and temperature on beam properties need to be investigated in a systematic manner.

Figure 1 visualizes isentropic jet expansions of carbon dioxide taking place in three different thermodynamic regimes. In a temperature–entropy phase diagram isentropic expansions are characterized by vertical trajectories. Expansion routes ‘A’ and ‘B’ both start at conditions well

0031-8949/09/048127+07$30.00

© 2009 The Royal Swedish Academy of Sciences Printed in the UK
The vapor pressure at this saturated liquid at a temperature of 273.15 K as suggested by the state of carbon dioxide \(^{('B')}\). In contrast, velocity distributions obtained in free jet droplets formed by condensation of the supersaturated vapor rationalized by clusters resulting either from droplets formed above the critical pressure \(P_c = 7.377 \text{ MPa}\) and the critical temperature \(T_c = 304.13 \text{ K}\). Pathway ‘C’ resembles the more usual experiment condition of a stagnation pressure up to a few hundred kilopascal. Both routes ‘A’ and ‘B’ originate from the supercritical state and reach the two-phase region. Their distinctive feature is that expansion ‘A’ passes the critical point on the liquid side, expansion ‘B’ on the vapor side. Interestingly, free jets emanating from stagnation conditions similar to ‘A’ and ‘B’ have been reported to exhibit dramatic differences in flow velocity as well as in cluster size \(^{10–13, 15}\). The latter observation has been rationalized by clusters resulting either from droplets formed by disintegration of the superheated liquid (‘A’) or from droplets formed by condensation of the supersaturated vapor (‘B’). In contrast, velocity distributions obtained in free jet expansions of supercritical fluids are still not understood in detail \(^{10, 12, 13, 15}\), and to this day are explained in the ineligible ideal gas model \(^{16}\).

In this paper, we employ the most advanced equation of state of carbon dioxide \(^{17}\) in order to numerically compute the relevant thermodynamic parameters, i.e. enthalpies and heat capacities. These data are used in different analytical expressions for the terminal flow velocity of supersonic beams of \(\text{CO}_2\). The different analytical expressions are obtained from a macroscopic description of an adiabatic expansion process, with varying degrees of simplifying assumptions. The pronounced dependence of the mean flow velocity on source pressure and temperature utilizing a new, universal description of real fluid systems is compared in detail with the three most widely applied approximations. Common conjectures in the mathematical description of supersonic jet expansions are discussed in detail. It is visualized that the usual supposition of ideal gas properties is quite inappropriate and results in severe errors, particularly so in the vicinity of the gas–liquid phase transition and the critical point.

## 2. Terminal flow velocities of free jets

In a macroscopic, thermodynamic picture, the free jet expansion of a fluid system into a vacuum can be described as an adiabatic process, provided that during expansion particle–wall interactions are negligible. In the absence of external fields the conservation of energy yields the following general relation for the flow velocity \(v_1\) of a collimated (one-dimensional) molecular beam:

\[
E = U_0 + P_0 V_0 + \frac{N_A m v_0^2}{2} = U_1 + P_1 V_1 + \frac{N_A m v_1^2}{2}.
\]

Here, the total molar energy \(E\) consists of the internal molar energy \(U\), describing the random translatational and internal motions of the particles, the pressure–volume work \(PV\) due to the change in molar volume \(V\) of the fluid occurring at a pressure \(P\), and the kinetic energy \(N_A m v^2/2\) resulting from the center-of-mass motion of \(N_A\) particles. This equation, and all equations derived from it, assumes a pure working fluid; accordingly, all particles have the same mass \(m\) and the same velocity \(v\). \(N_A = 6.022 \times 10^{23} \text{ mol}^{-1}\) is the Avogadro constant, and the index 0 marks the thermodynamic state of the fluid within the reservoir, prior to expansion, while the index 1 is used to describe the terminal properties of the beam. An implicit prerequisite for any practical application of this equation and any subsequent derivation is a thermal equilibrium between the particles and the reservoir walls, prior to expansion, permitting the assignment of a well-defined, uniform fluid temperature \(T_0\). Although this assumption might seem self-evident, it is of substantial experimental relevance. For example, it is well known that in converging nozzle geometries the working fluid may be compressed and heated significantly prior to expansion, see e.g. \(^{16, 19}\); hence in such cases a thermodynamic equilibrium between the fluid and the reservoir may not always be guaranteed, and the effective temperature of the fluid might deviate considerably from a measurement of a local nozzle temperature.

The deduction of an expression for the mean flow velocity of a supersonic jet that is more specific than \((1)\) requires another elemental—and occasionally disregarded—assumption: provided that the center-of-mass motion of the particles within the reservoir can be neglected, i.e. \(v_0 \simeq 0\), the total molar energy of the fluid in the reservoir is identical to its molar enthalpy: \(E = H_0 = U_0 + P_0 V_0\). This represents a convenient simplification, reducing \((1)\) to

\[
H_0 = H_1 + \frac{N_A m v_0^2}{2},
\]

with \(H_1 = U_1 + P_1 V_1\). However, the adiabatic expansion of pressurized gases through a long capillary or microchannels as...
frequently conducted in the various techniques of supercritical fluid technology [16] in general does not meet this seemingly marginal criterion. Therefore in applications where the flow velocity within the reservoir cannot be neglected the more general form

\[ H_0 + \frac{N_A m v_0^2}{2} = H_1 + \frac{N_A m v_1^2}{2} \]

should be adopted. The constraint of a center-of-mass motion \( v_0 \simeq 0 \) is equivalent to requesting a sufficiently small flux of particles leaving the stagnation volume and implies an insignificant disturbance of the thermodynamic equilibrium within the reservoir. While in general it may be difficult to judge if this condition can be approximated adequately in experiments, pulsed valves with a low duty cycle and a short opening time of a few microseconds [20] offer a minimized gas consumption and have proven to be advantageous in this respect. Thus in principle a negligibly small consumption of the working fluid can be realized, permitting the following approximate expression for the terminal mean flow velocity of the expanded particles:

\[ v_1(H_0, H_1) = \sqrt{\frac{2}{N_A m}} [H_0 - H_1]. \]  

(2)

Because the enthalpy of the liquid phase of a substance is smaller than the enthalpy of the vapor phase by the enthalpy of vaporization, \( \Delta_v H \), the flow velocity of the beam is not only affected by the source pressure and temperature, but first and foremost by the initial and final aggregation states of the molecules: the change of enthalpy \( H_0 - H_1 \), and hence the beam velocity \( v_1 \), is largest for a cold condensed jet resulting from the adiabatic expansion of a warm, uncondensed vapor. It is emphasized that (2) is valid for supersonic expansions of real gases as well as liquids and supercritical fluids. However, presumably because enthalpies are difficult to access, expression (2) is frequently transformed further using the relation:

\[ H_0 - H_1 = C_P [T_0 - T_1]. \]

(3)

Here the change of enthalpy caused by the expansion is linked to the temperature change of the fluid. \( T_0 \) denotes its temperature in the stagnation reservoir, \( T_1 \) the ‘temperature’ of the expanded jet, and \( C_P \) the molar heat capacity at constant pressure. However, relation (3) is valid only for a heat capacity that does not depend on temperature. This is a severe simplification, particularly due to the large temperature change achieved in a supersonic jet expansion. For helium, usually considered as a perfect gas, \( C_P \) changes by a factor of four in the temperature range of 3–300 K [21]. Hence, (3) is appropriate only for the model representation of an ideal gas, while for any real system it is a poor and questionable approximation. Even for rare gases at room temperature and low stagnation pressures (400–500 kPa), deviations from ideal gas behavior can be observed in experiments [22]. Moreover, the direct use of the molar isobaric heat capacity \( C_P \) will prohibit any reasonable description of first order phase transitions, and stagnation conditions close to the vapor–liquid phase boundary will inevitably result in gross errors of the calculated values. Surprisingly, these concerns are commonly ignored, arriving at

\[ v_1(T_0, T_1) = \sqrt{\frac{2C_P}{N_A m}} [T_0 - T_1]. \]  

(4)

Although this formula is regularly applied to real systems, it is valid only for ideal gases. Here, in the limiting case of a vanishingly small beam temperature, \( T_1 \ll T_0 \), the maximum flow velocity is given by

\[ v_{\text{max}}(T_0) = \sqrt{\frac{2C_P T_0}{N_A m}}. \]  

(5)

The implicit and somewhat hidden assumption of an ideal gas in this expression can be strengthened by adding the relation \( C_P - C_V = R \). This statement explicitly holds only for ideal gases, \( C_V \) being the molar heat capacity at constant volume, and \( R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1} \) the gas constant. In combination with the heat capacity ratio

\[ \gamma = \frac{C_P}{C_V}. \]

it is possible to avoid the direct and extremely problematic occurrence of the molar isobaric heat capacity \( C_P \) in the equations (4) and (5) by the substitution

\[ C_P = \frac{\gamma}{\gamma - 1} R. \]

Hence, assuming ideal gas properties, the flow velocity \( v_1 \) and the maximum flow velocity \( v_{\text{max}} \) can be expressed as

\[ v_1(T_0, T_1) = \sqrt{\frac{2R \gamma}{N_A m \gamma - 1}} [T_0 - T_1] \]  

(6)

and

\[ v_{\text{max}}(T_0) = \sqrt{\frac{2R \gamma T_0}{N_A m \gamma - 1}}. \]  

(7)

respectively. For an ideal monatomic gas, \( C_P = 5R/2 \), and (5) and (7) can be simplified:

\[ v_{\text{max}}(T_0) = \sqrt{\frac{5RT_0}{N_A m}}. \]

Originating from the same macroscopic picture of the free jet expansion of a fluid system into a vacuum, several different expressions have been derived. Although the three terms (2), (4) and (6) look rather similar, they are equivalent only in the hypothetical case of an ideal gas. Solely the universal model employing enthalpy changes, equation (2), should be applied to real gases, liquids and supercritical fluids.

3. Numerical results

In the following section, we investigate the pronounced influence of the fluid aggregation state on the maximum flow velocity of a supersonic beam, and the errors introduced by the various simplifications mentioned above. For these studies, the molecule carbon dioxide seems a perfectly
suitable model system due to its widespread utilization as a supercritical solvent at conditions where high stagnation pressures prevail. We thus calculate and visualize the largest possible flow velocity of neat CO$_2$ jet expansions as a function of stagnation pressure and stagnation temperature, and check the results from the different formulae against each other. All required thermodynamic quantities of carbon dioxide such as $H_0(P_0, T_0)$, $c_v(P_0, T_0)$ and $\gamma(P_0, T_0)$ are calculated numerically employing the real fluid equation of state developed by Span and Wagner [17]. Moreover, the pressure-independent flow velocity of a supersonic beam with a constant heat capacity ratio $\gamma = 9/7$, typically employed to describe rotating, linear molecules, is included in this comparison, too.

Before doing so, a reliable expression for the largest flow velocity $v_{\text{max}}$ in the generic enthalpy description of (2) needs to be developed. As mentioned above, the mean beam velocity $v_1$ is largest for a cold condensed jet resulting from the supersonic expansion of a warm vapor, due to the additional release of condensation energy. Because most equations of state, including [17], are limited to the fluid region, their lowest accessible temperature is given by the triple point temperature $T_t$. Consequently, within the parameter range available to this equation of state, the flow velocity in (2) is maximized for an enthalpy change that is at least as large as the enthalpy of vaporization, $\Delta_h H$. The maximum enthalpy of vaporization is encountered at the triple point. Hence, the maximum terminal flow velocity of a supersonic jet is obtained for a rest enthalpy that is given by $H_1 = H_{\text{liquid}}(P_t, T_t)$:

$$v_{\text{max}}(P_0, T_0) = \sqrt{\frac{2}{N_A m} \left[ H_0(P_0, T_0) - H_{\text{liquid}}(P_t, T_t) \right]}.$$  \hspace{1cm} (8)

$P_t$ is the vapor pressure at the triple point. Having deduced this formula, a detailed, systematic comparison of the three distinct model descriptions (5), (7) and (8) for the maximum flow velocity of an adiabatic jet expansion is now made possible, using the thermodynamic properties obtained numerically from the equation of state of CO$_2$. To begin with, the results corresponding to (8), i.e. the universal real fluid description with a rest enthalpy equivalent to a cold, liquid beam, are depicted in figure 2(A) for several characteristic source temperatures $T_0$. These computations reveal several interesting observations: firstly, in general the flow velocity decreases with increasing stagnation pressure, due to the enhanced particle associations in the reservoir. In consequence, the jet expansion of a liquid or a supercritical fluid yields a much reduced velocity in comparison to a gaseous system [23], assuming the same condensed end state. This is in sharp contrast to an ideal gas notion where only the temperature, and not the aggregation state, is relevant. Secondly, at source conditions corresponding to the vapor phase, flow velocities are remarkably higher than obtained for an ideal gas calculation, because the latter does not consider the possibility of cluster formation in the beam.

If condensation in the jet is less extensive than assumed in (8), the more general enthalpy difference $H_0 - H_1$ according to (2) has to be applied. Because the enthalpy change during the supersonic expansion can neither be directly accessed by experiment nor by simple calculations without introducing further assumptions, only specific, limiting cases can be considered within this universal real fluid description. Complementing the scenario of a complete condensation of the jet at a very low temperature, where $H_1 = H_{\text{liquid}}(P_t, T_t)$, as discussed above, is the limiting case of a supersonic beam without any cluster formation, hence $H_1 = H_{\text{superc}}(P_t, T_t)$. Here, the reference state is a gas at a low temperature and pressure, not a liquid as assumed in (8). Similarly, one could consider a case study providing a direct comparison with the approximate descriptions of the ideal gas model, (5) and (7): at zero stagnation pressure and at a reservoir temperature well above the gas–liquid phase transition, calculations employing (7) should yield results as reasonable as possible within the ideal gas picture. Hence, at $P_0 = 0$ both formulae (2) and (7) might be expected to yield comparable flow velocities. The combination of these two expressions then could be used to cautiously estimate the value of the enthalpy change at zero pressure for the particular case that no condensation in the expanding jet is assumed:

$$v_1(P_0 = 0, T_0) = \sqrt{\frac{2}{N_A m} \left[ H_0(P_0 = 0, T_0) - H_1 \right]} \approx \sqrt{\frac{2 R \gamma T_0}{N_A m \gamma - 1}}.$$  \hspace{1cm} (9)

This ‘reference value’ is indicated by a star in figures 2(A) and (B). The effect of this choice of a rest enthalpy on the resulting flow velocity is depicted in the lower curve of figure 2(B), while the upper curve is identical to the calculation at $T_0 = T_c$ in figure 2(A). In this way the range of possible velocities, depending on the amount of condensation in the jet, is illustrated by the shaded area. Because for CO$_2$ the vaporization energy is significant, the beam velocity is much smaller if no condensation in the jet is assumed. These two limiting cases of a cold liquid and a cold gaseous jet in figure 2(B) suggest a possibility to estimate the liquid fraction in the fully developed jet.

The major differences between the real fluid calculation of (8), depicted in figure 2(A), and the model of an ideal gas employing the heat capacity ratio (7), depicted in figure 2(D), are observed near the liquid–vapor phase transition and in the vicinity of the critical point. Computations relying on enthalpy changes yield a distinct step of the flow velocity at the vaporization line, while the use of the heat capacity ratio results in a less pronounced and remarkably broadened decrease of the beam velocity. Moreover, (7) predicts a noticeable minimum of the terminal flow velocity in the region of the critical point that cannot be found in the enthalpy model. Data obtained from the molar isobaric heat capacity description of (5) predict enormously large flow velocities at the phase transition and obviously elude any further discussion, see figure 2(C).

At $P_0 = 0$ and for temperatures well above the gas–liquid phase transition, where a real molecule is expected to behave as similar to an ideal gas as possible, (5) yields a flow velocity of 719 m s$^{-1}$ for $T_0 = T_c$, in full accordance with (7), indicating that the equation of state is self-consistent. Deviations at pressures $P_0 > 0$ thus can be ascribed to illegitimate model assumptions. This is further illustrated in
Figure 2. Terminal flow velocities $v_{\text{max}}$ of a supersonic beam of carbon dioxide, computed for a few characteristic stagnation temperatures $T_0$, including the gaseous, liquid and supercritical states. (A) Real fluid calculations employing (8) with a rest enthalpy of $H_1 = H_{\text{liquid}}(P_t, T_t)$, resembling complete condensation of the beam. Upper curve: real fluid calculation for $T_0 = T_c$ employing (8), i.e. a rest enthalpy of $H_1 = H_{\text{liquid}}(P_t, T_t)$, resembling complete condensation of the beam. (B) Lower curve: calculation for $T_0 = T_c$ employing (2) with a rest enthalpy $H_1$ defined via (9), resembling the ideal gas description at zero pressure. This scenario thus represents no cluster formation in the beam. Upper curve: real fluid calculation for $T_0 = T_c$ employing (8), i.e. a rest enthalpy of $H_1 = H_{\text{liquid}}(P_t, T_t)$, resembling complete condensation of the beam. (C) Calculations employing the molar heat capacity $C_p(P_0, T_0)$ according to (5), assuming ideal gas behavior. (D) Calculations employing the heat capacity ratio $\gamma(P_0, T_0)$ according to (7), assuming ideal gas behavior. Dash-dotted line in (A) and (D): calculation for $T_0 = T_c$ according to (7) with a constant heat capacity ratio $\gamma = 9/7$. 

Because all thermodynamic data are derived from the same equation of state, both the calculation employing molar enthalpies and the calculations employing the molar isobaric heat capacity or the heat capacity ratio should result in the same terminal flow velocities; differences may thus be attributed to the approximations in the derivations of (5) and (7).
4. Discussion and outlook

Since the early days of cluster research it has been observed experimentally that the mean beam velocity may increase with increasing stagnation pressure [24]. This phenomenon is frequently ascribed to cluster formation in the expanding jet [7, 24–27]. Apart from purely experimental challenges as discussed in section 2, in general the flow velocity of a supersonic beam will decrease with increasing source pressure due to a reduced enthalpy change caused by particle associations already in the stagnation reservoir. Simultaneously, however, nucleation and condensation in the expanding jet will increase, resulting in an increased enthalpy change and thus in an increased terminal flow velocity. Accordingly, the final beam velocity may decrease or increase with stagnation pressure, depending on stagnation temperature and vaporization energy.

In summary, we have presented a thermodynamic model providing a consistent physical picture for the supersonic jet expansion of real gases, liquids and supercritical fluids. The validity of frequently employed descriptions for the maximum flow velocity of supersonic beams has been critically reviewed. Because these mathematical terms are equivalent only for the model of an ideal gas, a direct comparison has been performed for the relevant case of a real world molecule, including its vapor, liquid and supercritical state. Pronounced differences are found for jet expansions originating from the vicinity of the gas–liquid phase transition or the critical point. More specifically, the use of the ideal gas model is defective for any system at elevated pressures. Particularly, formulae explicitly employing the molar heat capacity \( C_P \) should be avoided in that they yield unreasonable results for the terminal beam velocity of any non-ideal gas.

In consequence, a consistent thermodynamic picture is feasible only in terms of stagnation and beam enthalpy.

Most interestingly, the conclusion drawn from the calculations depicted in figure 2(A) is that it should be possible to determine experimentally, by measuring the velocity distribution of the expanding jet with high accuracy, the aggregation state of a substance within a reservoir. This insight could open up new vistas for molecular beams monitoring chemical compositions or (slow) processes such as phase transitions in real time. For example, in supercritical fluid technology typically a small fraction of a co-solvent such as ethanol is added to the supercritical carbon dioxide to enhance the solubility of more polar molecules in the non-polar solvent. In consequence, the critical point of this binary mixture shifts depending on the mole fraction of the co-solvent. This shift is difficult to predict theoretically and thus has to be determined by experiment. It might thus be convenient to actually observe this change of the critical temperature or pressure by an associated change in the mean flow velocity of the supersonic jet expansion.

Acknowledgments

We gratefully acknowledge valuable comments of the referee. This work was supported by the Deutsche Forschungsgemeinschaft (grant no. CH262/5).

References


[27] Sherman P M 1971 AIAA J. 9 1628