PHYSICAL REVIEW A **77**, 012702 (2008)

Cooling and slowing in high-pressure jet expansions

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(Received 10 August 2007; published 4 January 2008)

The mathematical term for the mean flow velocity in supersonic beams of ideal gases is extended to include real gas properties. This procedure yields an explicit dependence of the flow velocity on pressure, as observed in recent experiments of free jet expansions. Applied to stagnation conditions slightly above the critical point, the model suggests that seeded high-pressure jet expansions might be suitable for slowing down virtually any molecule with maximum efficiency. Moreover, we discuss the consequence of a pressure-dependent flow velocity v_0 for the speed ratio $S=v_0/\Delta v_\parallel$ with respect to collisional cooling and suggest to use the velocity spread $\Delta v_\parallel$ as a more nonambiguous measure of translational temperature in high-pressure jet expansions.

DOI: 10.1103/PhysRevA.77.012702 PACS number(s): 34.10.+x, 47.40.Ki, 51.30.+i, 82.60.Fa

I. INTRODUCTION

The experimental capability of cooling atoms has led to enormous progress in atom optics, ultracold physics, and Bose-Einstein condensation [1–5], disclosing a new world of research in condensed matter physics and quantum optics. Cooling molecules promises a similar manifold of scientific surprises and fundamental insights into chemical and physical interactions at low and ultralow temperatures [6]. Accordingly, the interest in cold and slow molecules is rapidly evolving [7–10], with the quest of establishing suitable techniques for their efficient generation. Besides a few rather specific methods such as the synthesis of molecules from cold atoms via photoassociation [11–14] or Feshbach resonances [15–17], general and powerful tools are available, employing either molecular collisions with a cryogenic buffer gas [18–22] or the strong adiabatic cooling in free jet expansions [23–25]. As a consequence, several approaches take advantage of the unique combination of versatility, high particle density, and narrow velocity spread provided by supersonic beams, producing molecules that mostly reside in their lowest rotational and vibrational state. So far, the challenge of decelerating (part of) the expanding beam has been tackled by using electric [26–42], magnetic [43–46], or optical [47–52] fields, "billiardlike" collisions in crossed molecular beams [53,54], a moving beam source [55,56] or a moving scattering surface [57].

Quite in contrast to these distinct efforts, the influence of real gas properties such as phase transitions on the terminal flow velocity has not yet been investigated. This is particularly true for supersonic beams from the supercritical state with its unusual and very exciting physical and chemical properties. Also because the velocity dispersion in supersonic beams can be significantly reduced with increasing stagnation pressure [58–60], it is essential to gain some insight into the thermodynamics of high-pressure jet expansions.

While the adiabatic and isentropic expansion of an ideal gas into vacuum may be easily explained [61], a real gas such as carbon dioxide, in particular at higher stagnation pressures, presents a much more complicated situation. Hence, very basic questions such as the relevance of the thermodynamic parameters stagnation pressure p_0 and stagnation temperature T_0 for translational cooling in high-pressure jet expansions need to be investigated, both experimentally and theoretically.

One of the prime questions in this respect is an appropriate figure of merit for translational cooling in supersonic beams. Because the beam temperature as the measure of random molecular motion is not a directly accessible quantity, the experimentally more convenient velocity dispersion $\Delta v_\parallel$ can be used as a suitable characteristic parameter. For an ideal gas it is related to the translational temperature $T_\parallel$ via

$$\Delta v_\parallel = \sqrt{\frac{2k_B T_\parallel}{m}},$$

where k_B is Boltzmann's constant and m is the molecular mass. More frequently, however, the speed ratio

$$S = \frac{v_0}{\Delta v_\parallel}$$

is employed to quantify the translational cooling of a supersonic beam with a mean flow velocity v_0. As we will demonstrate below, it may not always be a proper choice.

II. MODEL

Assuming a stationary, adiabatic and reversible (and hence isentropic) expansion of a perfect gas into vacuum, its maximum, terminal flow velocity v_0 is given by

$$v_0(T_0) = \sqrt{\frac{2k_B T_0}{m}\frac{\gamma}{\gamma-1}}, \tag{1}$$

provided that the initial stagnation enthalpy of the gas is completely converted into directed translational motion. Here, $\gamma = C_P/C_V$ is the ratio of the heat capacities at constant pressure C_P and constant volume C_V, depicting the capability of the expanding gas of performing work.

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For an ideal gas, the flow velocity v_0 depends on stagnation temperature, but not on stagnation pressure. In the case of constant temperature T_0, the speed ratio S is inversely proportional to the velocity dispersion $\Delta v_\parallel$ and hence presents a suitable figure of merit for the translational cooling in supersonic beams; a large speed ratio is equivalent to a small velocity spread.

For any real system, however, the gas density *does* influence the mutual particle interactions and therefore results in a pressure-dependent heat capacity ratio. This is true even for rare gases such as argon. In consequence, the flow velocity is affected by the stagnation pressure as well, and we introduce a generalizing modification of Eq. (1),

$$v_0(p_0,T_0) = \sqrt{\frac{2k_B T_0}{m}\frac{\gamma(p_0,T_0)}{\gamma(p_0,T_0)-1}}. \tag{2}$$

Here, the temperature- and pressure-independent value of the heat capacity ratio γ has been replaced by a more realistic function $\gamma(p_0,T_0)$, which can be calculated from tabulated values [62] of the heat capacities $C_P(p_0,T_0)$ and $C_V(p_0,T_0)$. It is plotted in Fig. 1 for Ar and CO_2. According to these data, the change of the heat capacity ratio with stagnation pressure can be quite significant. The deviations from the ideal gas value are most distinct in the close vicinity of the critical point.

The equipartition of energy in classical statistical mechanics relates the heat capacity C_P with the number of degrees of freedom f of the expanded gas, $C_P=(f+2)R$; $R=8.3145\ \mathrm{J\ mol^{-1}\ K^{-1}}$ is the gas constant. Therefore the macroscopic property C_P can be correlated with the internal motion and molecular structure of the particles. The divergent value of C_P at the critical point can thus be interpreted as a large scale fluctuation, i.e., collective motion of particles. Phrased differently, the random motion of individual particles is minimized, offering a possible explanation for the recent observation of extremely cold molecular beams from supercritical fluids [60].

III. RESULTS

The effect of real gas properties and hence the stagnation pressure on the resulting flow velocity v_0 can be evaluated using Eq. (2). The result is visualized in Fig. 2 for argon and carbon dioxide at a constant stagnation temperature $T_0=325$ K. For comparison, the terminal flow velocity of an ideal gas according to Eq. (1) is shown as well. At very low stagnation pressures argon can be treated as an almost ideal gas and indeed both results coincide. Interestingly, the decrease of v_0 with increasing p_0 has been observed for Ar even at low pressures in recent high resolution experiments [63]. The reduced terminal velocity observed at elevated stagnation pressures could be rationalized by the decrease of stagnation enthalpy due to enhanced particle associations in the high-pressure reservoir.

The proposed model may even be applied to the very special case of helium at low temperatures, as realized in cryogenic free jet expansions [64]. Figure 3 visualizes the dependence of the mean flow velocity v_0 of He on the stagnation pressure p_0, for the three different temperatures investigated in Ref. [64]. Our model calculations obtain both the initial decrease and the subsequent increase of v_0 with increasing pressure, as reported in the experiments [64].

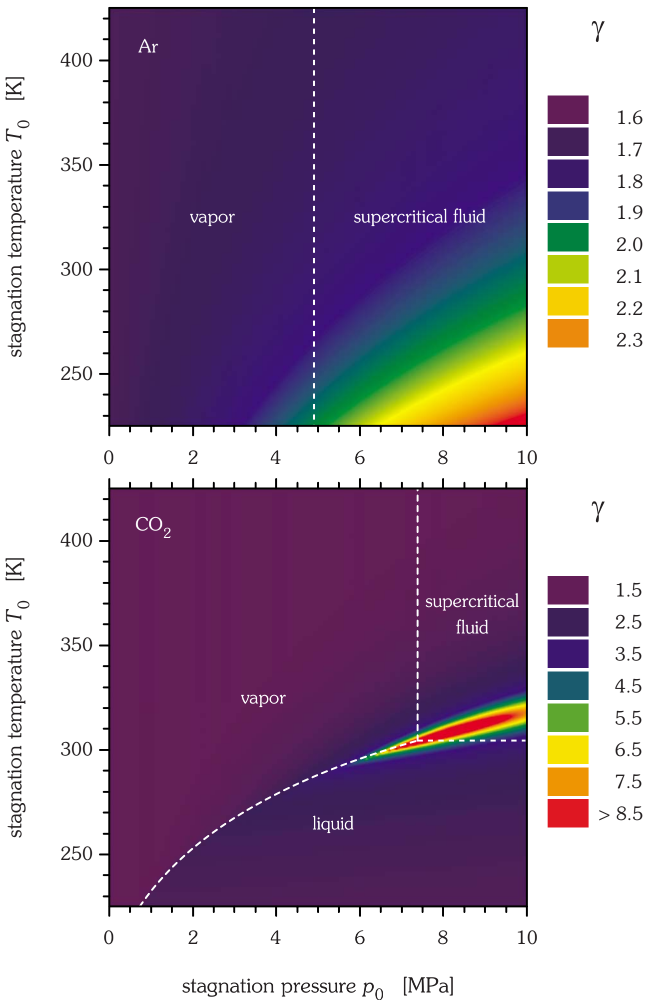

FIG. 1. (Color online) Heat capacity ratio $\gamma(p_0,T_0)$ of Ar (top) and CO_2 (bottom), calculated using tabulated heat capacities $C_P(p_0,T_0)$ and $C_V(p_0,T_0)$. The displayed pressure and temperature range is accessible to high resolution molecular beam experiments [60,63]. The dashed white lines mark the phase boundaries. For comparison, an ideal monoatomic gas with three translational degrees of freedom is characterized by $\gamma=5/3$, a linear, triatomic molecule with $f=7$ degrees of freedom by $\gamma=9/7$. For Ar, the critical point is located at $p_c=4.863$ MPa and $T_c=150.69$ K, for CO_2 at $p_c=7.377$ MPa and $T_c=304.13$ K [62].

While for rare gases far from their phase transitions Eq. (2) predicts a slight decrease of the flow velocity v_0 of a few percent only, for real gases such as CO_2 the calculated drop in velocity may be quite dramatic. For a pressure change from 0 to 10 MPa, the flow velocity of Ar decreases by 8%, whereas for CO_2 the slowing of the beam reaches 48%. Within the scope of this model, an increased stagnation pressure thus could be used to efficiently generate slow and very intense beams of cold molecules. The appealing features of this prediction are that (i) due to the supersonic expansion

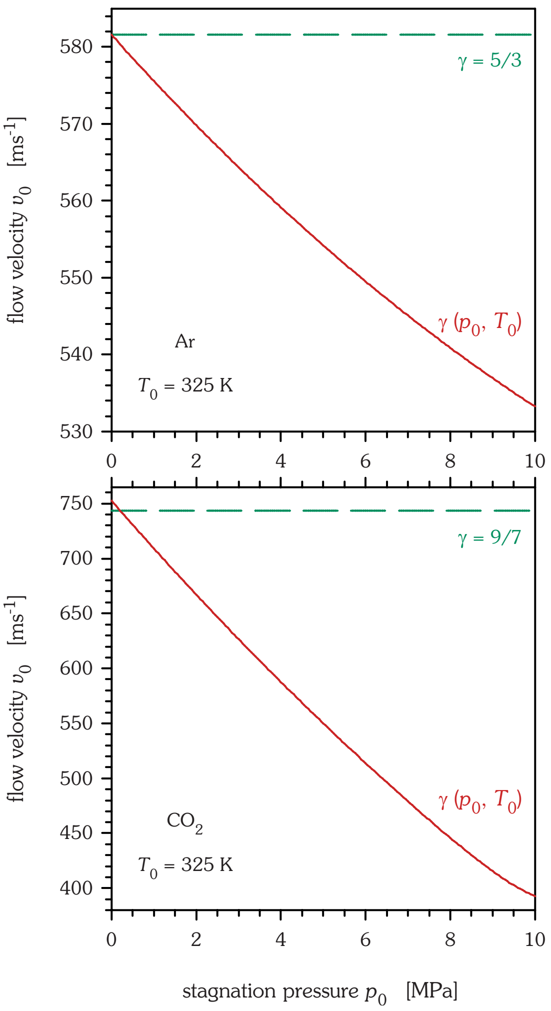

FIG. 2. (Color online) Terminal flow velocity of a supersonic beam at a constant stagnation temperature of T_0=325 K. Top: Green dashed line, prediction of Eq. (1) for a monoatomic gas with γ=5/3 and the mass of Ar, m=39.95 amu. Red solid line, prediction of Eq. (2) for argon atoms, with $\gamma(p_0,T_0)$ (see Fig. 1). Bottom: Green dashed line, prediction of Eq. (1) for a linear, triatomic gas with γ=9/7 and the mass of CO$_2$, m=44.01 amu. Red solid line, prediction of Eq. (2) for carbon dioxide molecules, using $\gamma(p_0,T_0)$ (see Fig. 1).

not only the translational [60], but also the internal degrees of freedom of the molecules are strongly cooled, and (ii) the method is available for virtually *any* molecule. For the most efficient *slowing* of the beam we thus suggest to dilute the molecule of interest in a beam of supercritical Xe (or SF$_6$), which due to its large mass results in velocities below 200 ms^{-1}, see Fig. 4. Using suitable supercritical fluids, even nonvolatile or thermally labile molecules are accessible to molecular beams as has been demonstrated recently for caffeine [65]. While comparably small flow velocities $v_0 \gtrsim 224$ ms^{-1} can be obtained by expanding gaseous xenon at very low temperature ($\gtrsim$165 K) and pressure ($\simeq$100 kPa), the cooling efficiency of high-pressure jet expansions [60] is lost under those conditions. Consequently, huge velocity spreads of $\Delta v_{\parallel}$=45–60 ms^{-1} are reported [26,31]. It should be emphasized that in supersonic beams of supercritical fluids *all* particles would be slowed down in a similar way. This is substantially different from cooling schemes employing time-varying fields where typically only a small subset of molecules is decelerated.

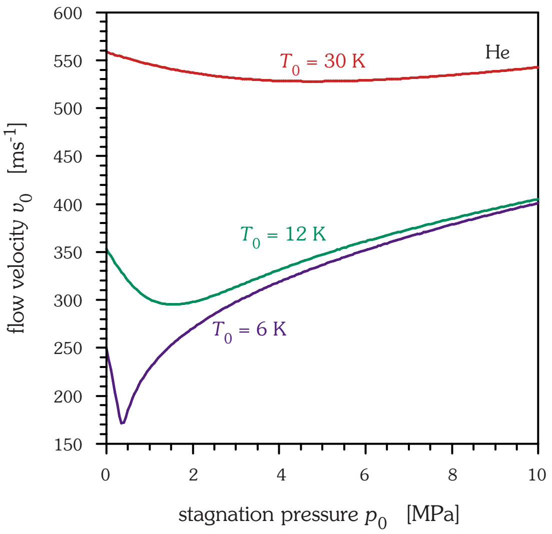

FIG. 3. (Color online) Terminal flow velocity v_0 of a supersonic He beam, calculated for three stagnation temperatures T_0=6 K, T_0=12 K, and T_0=30 K, using Eq. (2) with m=4.00 amu and $\gamma(p_0,T_0)$. Both the decrease and the subsequent increase of v_0 with increasing stagnation pressure p_0 observed in the experiments [64] are found in the calculations.

While calculations based on Eq. (2) do not directly provide a microscopic picture e.g., of condensation processes,

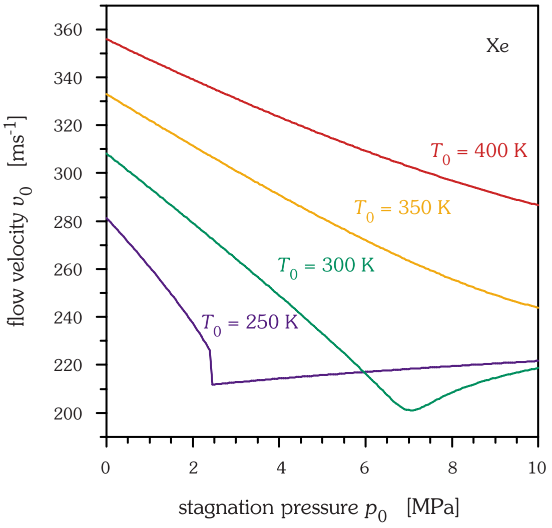

FIG. 4. (Color online) Pressure-dependent flow velocity v_0 of a supersonic Xe beam, calculated for different stagnation temperatures using Eq. (2) with m=131.29 amu and $\gamma(p_0,T_0)$. At higher temperatures, xenon is in the gaseous state and the flow velocity decreases with increasing pressure. At T_0=300 K, the region close to the critical point with large heat capacities is approached, leading to a remarkable minimum in v_0. For T_0=250 K, the phase transition between gas and liquid results in a sudden drop in the flow velocity.

the model does, however, include a phenomenological pressure dependence, reflecting the distinct changes of the heat capacities at the phase boundaries. This feature is completely absent in the commonly used expression (1).

How does a pressure-dependent flow velocity affect the characterization of translational cooling in high-pressure jet expansions? Let us assume a supersonic beam of CO_2 with a constant translational temperature $T_{\parallel}$, and hence with a constant velocity dispersion $\Delta v_{\parallel}$. The decrease of the flow velocity v_0 as seen in Fig. 2 then implies a speed ratio that drops by nearly 50%, if the stagnation pressure is increased from 0 to 10 MPa. The usual interpretation of the speed ratio in terms of translational cooling would suggest a substantially reduced cooling efficiency [59]. At these pressure conditions this observation could very reasonably be explained by condensation processes. Here however, the decrease of S with increasing pressure is only due to the definition of the speed ratio, and not related to any change in the velocity spread. Thus we conclude that the speed ratio may not be a good measure for translational cooling if the flow velocity is significantly affected by stagnation pressure.

IV. SUMMARY

In summary, a straightforward extension of the formula for the flow velocity of a perfect gas reveals a significant dependence of v_0 on stagnation pressure. This result suggests that high-pressure supersonic jets could provide an exceptionally versatile method for the efficient generation of intense, slow, and extremely monochromatic molecular beams. Due to the outstanding phase-space density of compressed gases this approach should be of particular relevance for any further deceleration scheme employing supersonic expansion sources. Moreover, our model reveals that the speed ratio S does not unambiguously reflect translational cooling. We therefore recommend the use of the velocity dispersion $\Delta v_{\parallel}$ as a more suitable figure of merit for translational cooling in supersonic beams, at least in cases of significant pressure changes.

ACKNOWLEDGMENT

This work has been supported by the Deutsche Forschungsgemeinschaft (Grant No. CH262/5).

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