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Kinetic Description of the Expansion of a Supersonic Pulsed Jet into a Vacuum: III. Determination of the Parameters of the Atomic Interaction Potential at Low Temperatures

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Abstract—A new method based on the kinetic description of a supersonic pulsed jet is proposed for the determination of the parameters of the atomic interaction potential. Analytical relationships are established between the peak position of the observed time-of-flight spectrum, on the one hand, and the source conditions and interaction potential parameters, on the other.

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Supersonic pulsed jets and molecular beams have been used in various fields of physics and chemistry; in particular, the jet property of experiencing deep cooling in reciprocating and internal degrees of freedom is widely used. This property makes it possible to determine the kinetic coefficients of a gas at low temperatures down to 1 K.

A method was developed for the determination of the atomic interaction potential from the parameters of a steady supersonic jet (the kinetic temperature and velocity slip) measured as functions of the jet-source conditions (pressure, temperature, nozzle size, and gas composition) [1–5]. The details of this method as applied to pure inert gases and their mixtures are described in [6]. The molecular beam parameters are determined using a time-of-flight method, which makes it possible to measure the time-of-flight spectrum, restore the distribution function from this spectrum, and obtain all moments of the distribution function (density, mean velocity, and temperature). Supersonic pulsed jets can also be treated in this manner (experimental setups with supersonic pulsed jets are one to two orders of magnitude cheaper and more compact than setups with steady jets). However, the restoration of the distribution function from the time-of-flight spectrum requires the solution of an integral equation of the convolution type, which is an ill-posed problem [7]; this means that even a small noise in the spectrum can give rise to a great error in the restored function. The numerous existing regularizing algorithms require the exact knowledge of the instrumental function, which is in most cases impossible, and a satisfactory accuracy is only achieved with a great distortion of the real distribution function [8].

Here, we propose a base for the determination of the parameters of the atomic interaction parameters from the kinetic description of supersonic pulsed jets [9, 10]. The atomic interaction potential parameters can be derived from the time-of-flight spectrum, namely, from the instantaneous particle density as a function of time.

Fundamental Relations

In the derivation of the fundamental relations, we will use the following mathematical model of a time-of-flight experiment: at the moment of closure of the pulsed valve ($t = 0$), the gas packet starts to travel in the direction of the detector and passes the time-of-flight base with length L_0, which is the distance from point r_s [9] to the detector. The detector cuts a cylinder with base y_0 (y_0 is the inlet diameter of the detector) from the gas packet and detects the inlet-surface-average instantaneous density $N_\alpha(t)$ of α-type particles. At moment t,

$$N_\alpha(t) = 2y_0^{-2}\int_0^{y_0} n_\alpha(\vec{r}, t)\, y\, dy, \qquad (1)$$

where $r = [(L_0 - u_{\lim}t)^2]^{1/2}$, and $n_\alpha(\vec{r}, t)$ and $u_{\lim}$ are defined in [9, 10].

$t_{\alpha\alpha}^{\max}$, the maximum position of the time-of-flight spectrum for the α component of the mixture, can be determined experimentally with a good accuracy. The expression for $t_{\alpha\alpha}^{\max}$ was derived from the equation $dN_\alpha(t)/dt = 0$. For a one-component beam, using

expressions for $n_\alpha(\vec{r}, t)$ {see Eqs. (19) and (10) in [9]}, we have

$$t_{\alpha\alpha}^{\max} - A = (p_0^0)^{-\frac{2n}{3n-4}} C_{n,\alpha\alpha}^{-\frac{A}{8n-4}} B. \quad (2)$$

Here, p_0^0 is the source pressure, $C_{n,\alpha\alpha}$ is the constant of the interaction potential, $V_{\alpha\alpha}(r) = -C_{n,\alpha\alpha}/r^n$, and A and B are functions of L_0 and the source conditions. Being cumbersome, they are not given here (see [11]). Here, all quantities are dimensional.

Next, from the starting data (the source temperature, gas molecular weight, and setup geometry), we calculate A and B. Then, n and the force constant $C_{n,\alpha\alpha}$ can be determined from $t_{\alpha\alpha}^{\max}$ as a function of p_0^0 in the log–log space.

The method can also provide data on the interaction potential of dissimilar particles. To obtain such data, we should roughly determine $n_\alpha(\vec{r}, t)$ from the Knudsen number Kn_s [10]:

$$n_\alpha(\vec{r}, t) = n_0 y_0^0 Kn_s^{\frac{2n}{3n-4}} (n_1 y_\alpha^0 + n_0 y_\alpha^1).$$

To calculate y_α^1, we should know the velocity slip $\Delta w_{\alpha,\beta}$. Simple but cumbersome transformations result in an expression for the shift of the component density peaks, which is suitable for data processing:

$$t_{\alpha\beta}^{\max} = D^{-\frac{3n}{3n-4}} C_{n,\alpha\alpha}^{-\frac{4}{3n-4}} C_{n,\alpha\beta}^{-\frac{2}{3n-4}} (t_{\alpha\alpha}^{\max} - A). \quad (3)$$

Expression (3) determines $C_{n,\alpha\beta}$ from experimental data, as for a one-component gas. D, as A or B, depends on the nozzle conditions and the setup geometry.

Lastly, let us determine the applicability limits of the method. Expressions (2) and (3) for the peak position of the time-of-flight spectrum account for the contribution from the particles received by the detector directly from the source. Therefore, the experiment should exclude the detection of background particles received by the detector after scattering by the walls of the vacuum chamber (a secondary signal). Let the characteristic size of the working volume of the vacuum chamber be l_0. The size of the gas packet R_0 after it flights base distance L_0 can be estimated at

$$R_0 = R_s + (5RT_s)^{1/2} (5RT_0^0)^{-1/2} L_0 \cong R_s + 0.3L_0.$$

From the nondisturbance of the main signal by the secondary one ($R_0 \le l_0$) and with account for the expression for R_s [9], we can determine the upper boundary for the nozzle operation time as

$$\tau_0 \le \tau_0^{\max} = 7.8 \times 10^{-6} (l_0 - 0.3L_0)^3 d^{-2}.$$

In real experimental settings ($d \cong 0.01$ cm, $l_0 \cong 10$ cm, and $L_0 \cong 30$ cm), $\tau_0^{\max}$ is on the order of a second. Moreover, from the expression for $\tau_0^{\max}$, base distance L_0 should not exceed ~$3l_0$ to exclude the appearance of a background signal.

On the other hand, there should be a lower bound of τ_0 that ensures the existence of a near-continuum regime at point r_s near the nozzle, where the gas packet is generated [9]. To find it, we should set the maximal Knudsen number value at point r_s that still ensures the near-continuum regime. From the numerical solution of the Boltzmann's equation for this problem [11], we can set with an acceptable accuracy that $Kn_s \le 5 \times 10^{-3}$. This gives us the lower bound for τ_0:

$$\tau_0 \ge \tau_0^{\min} = 3 \times 10^{-9} d (p_0^0 d)^{-3}.$$

In so doing, we set that $T_0^0 = 300$ K. For typical conditions ($d = 0.01$ cm and $p_0^0 = 1$ atm), $\tau_0^{\min} = 30$ μs. Interestingly, estimates for the same conditions performed in [12, 13] gave a close value (~20 μs).

We should emphasize that the method exploits the model of a spherical gas packet generated at a certain distance r_s that ensures continuality. These assumptions, however, do not seem very strained for the following reasons. First, for rather long times of expansion ($t \gg \tau_0$), the gas packet forgets the initial conditions and its initial shape approaches a sphere [14]. Second, usually, $r_s \ll L_0$ and the linkage site does not affect the final result.

To summarize, we have developed the fundamentals of a new method for the determination of the atomic interaction potential parameters in terms of the kinetic model of the expansion of pulsed beams of one-component gases and their mixtures. We derived analytical relations between the peak position of the time-of-flight spectrum, on the one hand, and the jet-source conditions and the interaction potential parameters, on the other. The applicability of the method regarding variable experimental parameters and setup geometry has been determined.

REFERENCES

1. Kuleznev, E.V., Lazarev, A.V., and Trubnikov, D.N., *Vestn. Mosk. Univ., Ser. 2: Khim.*, 1987, vol. 28, p. 117.
2. Lazarev, A.V., Kuleznev, E.V., and Trubnikov, D.N., *Vestn. Mosk. Univ., Ser. 2: Khim.*, 1988, vol. 29, p. 157.
3. Lenin, L.V., Lazarev, A.V., and Trubnikov, D.N., *Chem. Phys. Lett.*, 1988, vol. 148, p. 401.
4. Lazarev, A.V., Larin, A.V., and Trubnikov, D.N., *Khim. Fiz.*, 1992, vol. 11, p. 21.
5. Lazarev, A.V., Zastenker, N.N., and Trubnikov, D.N., *Vestn. Mosk. Univ., Ser. 2: Khim.*, 2004, vol. 45, p. 177.

6. Trubnikov, D.N., *Doctoral (Chem.) Dissertation*, Moscow, 1992.
7. Tikhonov, A.N. and Arsenin, V.L., *Metody resheniya nekorrektnykh zadach* (Solutions of Ill-Posed Problems), Moscow, 1986.
8. Voskoboinikov, Yu.E., Preobrazhenskii, N.G., and Sedel'nikov, A.I., *Matematicheskaya obrabotka eksperimenta v molekulyarnoi gazodinamike* (Mathematical Processing of Molecular Gas Dynamic Experiments), Novosibirsk, 1984.
9. Lazarev, A.V., Zastenker, N.N., Trubnikov, D.N., Tatarenko, K.A., and Pribytkov, A.V., *Vestn. Mosk. Univ., Ser. 2: Khim*., 2006, vol. 47, p. 377.
10. Lazarev, A.V., Zastenker, N.N., Trubnikov, D.N., Tatarenko, K.A., and Pribytkov, A.V., *Vestn. Mosk. Univ., Ser. 2: Khim*., 2007, vol. 48, p. 235.
11. Kolosova, T.Yu., *Cand. Sci. (Chem.) Dissertation*, Moscow, 1990.
12. Saenger, K.L., *J. Chem. Phys.*, 1981, vol. 75, p. 2467.
13. Saenger, K.L. and Fenn, J.B., *J. Chem. Phys.*, 1983, vol. 79, p. 6043.
14. Greenspan, H.P. and Butler, D.S., *J. Fluid Mech.*, 1962, vol. 13, p. 101.