While he did not suggest a physical explanation for the microstructural change, it is not difficult to envision that low energy cluster deposits form a porous material structure while individual atoms at a higher temperature create a denser microstructure (Fig. 2.5).

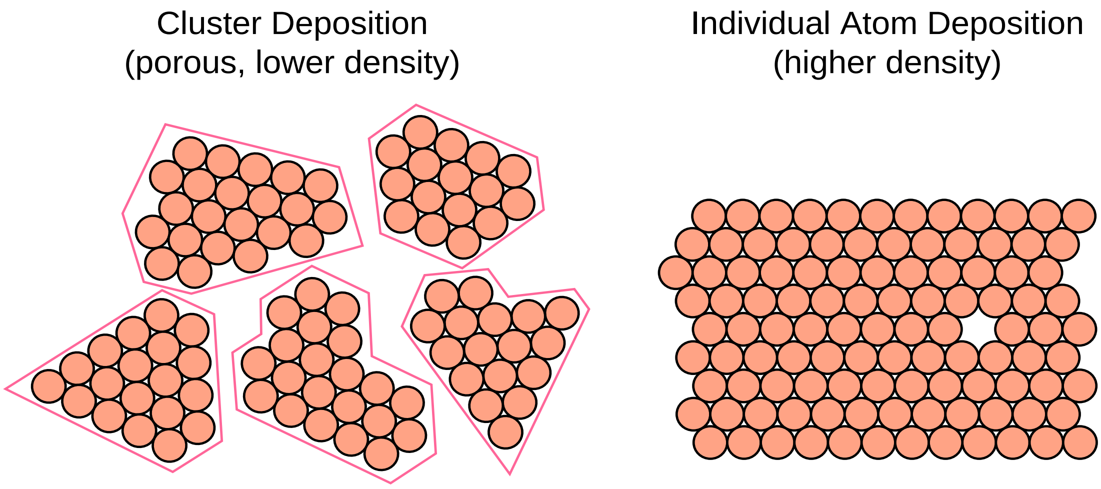

Figure 2.5 **The effect of clustering upon deposited film morphology.** A hypothetical comparison between the film structure formed during low energy cluster deposition and higher energy individual atom deposition.

2.2.3. Jet Vapor Deposition^{TM}

During the 1980's a new method was invented for creating films in a reduced vacuum and for manipulating vapor stream characteristics (i.e. distribution, energy, angle, efficiency, and form) during transport from source to substrate [47, 85]. Jet Vapor Deposition™ (JVD™) used a nozzle and gas jet to transport atoms or clusters of atoms to a substrate for deposition. This technique represents an extension of the technology of high pressure ratio molecular beam separators to a lower pressure ratio regime [101-110].

JVD™ often employs either a thermal evaporation source (a resistively heated wire) or another non-electron-beam heating source in combination with an inert gas jet to create vapor atoms, to accelerate those atoms from their thermally induced velocities, to concentrate the vapor stream through a spray nozzle, and to deposit the adatoms onto a substrate in a low vacuum (~ 10^{-2} Pa) (Fig. 2.6) [9, 10, 12]. JVD™ employs vapor atom collisions

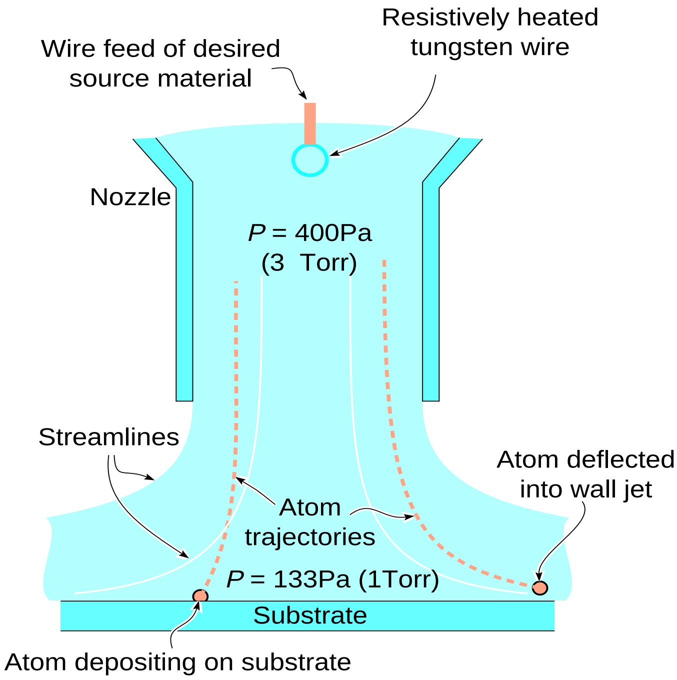

Figure 2.6 **Molecular beam deposition.** Once vapor atoms are accelerated through a nozzle, they can either impinge upon the substrate or be deflected into the wall jet. The pressure ratios shown are representative of those employed in a JVD™ system [12, 79].

with a carrier gas flowing towards the nozzle exit to redirect the vapor and reshape the vapor's density distribution. Using a pressure drop into the chamber to accelerate the entire flow, the JVD™ method then makes use of the inertial momentum of the vapor atoms to create a focussed deposit since, for a critical range of pressures, many of the vapor atoms cannot be turned into the wall jet by atomic collisions with the carrier gas before contacting the substrate (Fig. 2.6).

Reported results from deposits created with molecular beam separators and JVD^{TM} processes suggest that they could have a unique ability to vary vapor atom spatial, angular, and energy distributions as well as deposition efficiencies and vapor atom forms [47, 80, 83, 101-112]. Though not reporting exact distribution information, JVD^{TM} results indicate that, by using a high molecular weight vapor atom / low molecular weight carrier gas combination (e.g. gold / helium), focussed, highly efficient, highly nonuniform deposits can be created on stationary substrates [47]. While reporting focussed, high deposition efficiencies for gold on flat substrates (95%), Halpern et al. [47] and others [113, 114] do not provide information on the exact vapor atom spatial, angular, or energy distributions during transport and deposition. Hill [79] does present limited fiber coating deposition distribution data for the JVD^{TM} process with basic continuum-based model explanations for the observed experimental results. In other modeling work related to the JVD^{TM} process, de la Mora et al. [115] and Marple et al. [104] use continuum fluid flow concepts such as Stokes number and drag coefficient to examine the influence of vapor cluster mass upon deposition efficiency. Little in-depth analysis appears to be available in the literature though for a complete assessment of the rapid material synthesis abilities of these low pressure molecular beam systems.

In addition to an ability to affect vapor atom deposition efficiency and distribution, molecular beam separators and the JVD^{TM} process could have the ability to increase adatom kinetic energy by passing the vapor through a nozzle. First order estimates of the maximum velocity attainable through use of a nozzle can be determined using one-dimensional equations for isentropic flow of a compressible fluid [116]. The important governing relationships between pressure, temperature, Mach number, and jet velocity are given by:

$$\frac{P_o}{P_d} = \left[1 + \frac{\gamma - 1}{2}M^2\right]^{\gamma/(\gamma - 1)} \tag{2.19}$$

and

$$U = M\sqrt{\gamma R_s T} \tag{2.20}$$

where P_o = Upstream pressure before the nozzle (Pa),

P_d = Downstream pressure at the nozzle or in the chamber (Pa),

γ = Ratio of specific heats (5/3 for helium and argon),

M = Flow's Mach number,

U = Carrier gas stream speed (m/sec),

T = Absolute temperature (K), and

R_s = Specific gas constant (2077 J/(kg K) for helium, 208.1 J/(kg K) for argon).

2.2.4. Supersonic gas jet structure

While equations (2.19) and (2.20) give an upper bound to vapor atom velocity and kinetic energy exiting a molecular beam nozzle, multidimensional shock waves further downstream in low vacuum supersonic gas jets slow the carrier gas from supersonic velocities as the gas and vapor travel toward the substrate [117], making vapor atom velocity and position prediction with these one-dimensional equations impossible (Fig. 2.7). Two of the most important features of a supersonic nozzle expansion are the so-called zone of silence, where the gas flow accelerates to supersonic velocities, and a Mach disk, at which the gas flow rapidly decelerates to velocities below Mach 1 (Fig. 2.7). In addition to these structures, Adamson and Nicholls and others [117, 118] note that when a supersonic jet exits into a low vacuum (above a pressure of ~1 Pa), weak secondary shock structures can be present downstream of the sharply defined Mach disk.

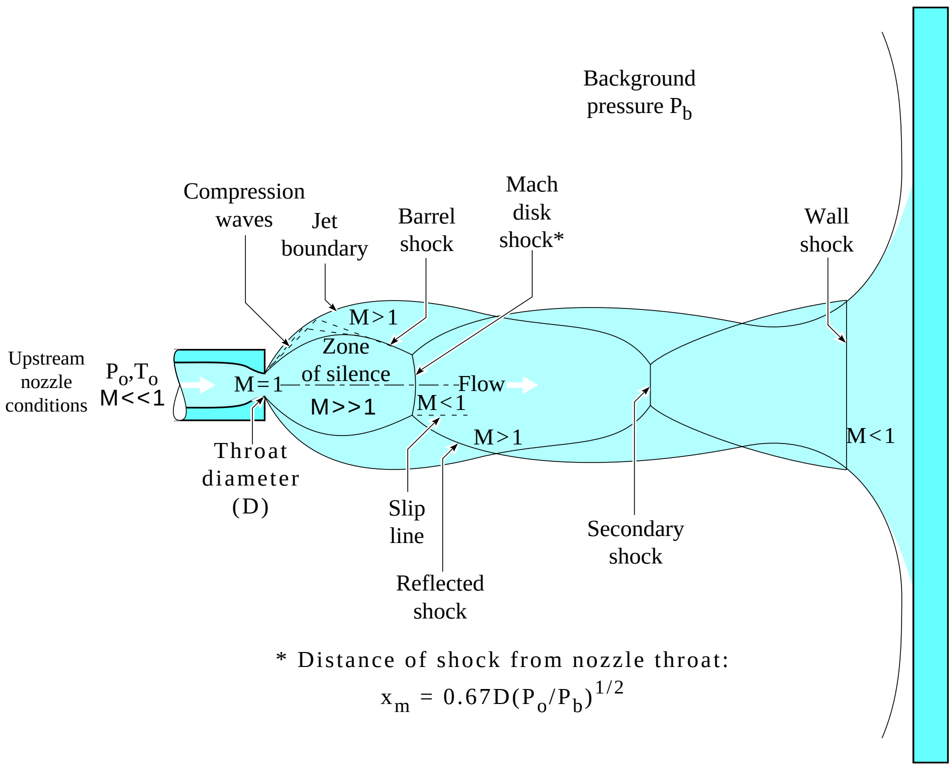

Figure 2.7 **Structure of a continuum free-jet.** The general structure of a continuum free-jet expansion has been well characterized [117-120]. The structure shown here is considered to be continuum-based since its existence requires a high enough density and collision frequency to allow for the definition of density and equilibrium temperature within the length scale of the apparatus [118].

The initial, expanding zone of silence is formed when the “high” pressure gas in the nozzle enters the chamber and expands in an attempt to match the lower background pressure found in the processing chamber. In many instances in which the background pressure is high enough to allow for a continuum description of atomic interaction, the nozzle exhaust overexpands, creating a lower pressure in the zone of silence than that found in the surrounding chamber. As a result, the background pressure forces the overexpanded barrel shock to narrow.

At some point downstream, the compression waves surrounding the barrel shock coalesce to generate a diamond shock or a Mach disk shock if the pressure ratio (P_o/P_d) is significantly above the level necessary to generate supersonic flow (2.05 for helium and argon). Depending upon the pressure in the processing chamber, this expansion and contraction sequence can be repeated as the jet attempts to reach equilibrium with the surrounding gas. Subsequent shock waves beyond the initial Mach disk are of decreasing strength as viscous effects dissipate the jet's energy [117]. While the zone of silence represents the primary region of supersonic flow, the repeated expansions of the jet downstream can create small additional regions of supersonic flow. The final major feature of the flow is the wall jet. Once the gas flow interacts with the substrate, the speed of the gas jet toward the substrate slows dramatically, a concave wall shock forms, and the gas is forced parallel to the substrate [120]. In sum, the idea of using a carrier gas stream to facilitate vapor deposition appears intriguing, but the technique is not well characterized or understood.

Interaction of the vapor atoms and carrier gas with the substrate undoubtedly decreases the adatom velocity component directed toward the substrate as the vapor atoms are redirected into the wall jet (c.f. Fig. 2.6). While the correlation between velocity and kinetic energy for vapor atoms of selected mass is simple ($E = \frac{1}{2}mv^2$), little experimental or theoretical work has been done to determine the actual velocity of adatoms reaching the surface in a vapor deposition system utilizing a nozzle and gas jet.

2.2.5. Vapor transport modeling

Because of the development of low and medium vacuum technologies such as diode sputtering and JVD^{TM}, theoretical understanding of vapor transport for materials processing has become a point of focus in recent years. Numerous researchers have investigated vapor transport issues in these systems and have realized that modifications to initial