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Fluctuations in Superdense and Supercritical Systems: A van der Waals Perspective

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Abstract: We present new insights into the van der Waals (vdW) model, focusing on two key aspects: 1) the concept of maximum possible density (MPD) $n = 1/b$, and 2) the Fano factor's role in analyzing supercritical fluids and also in determining limits on the applicability of the van der Waals approach. Our aim in these investigations is to bridge the complexity of statistical mechanics with practical applications, targeting researchers and engineers in thermodynamic modeling and supercritical fluid systems. Our MPD, derived from the vdW excluded volume parameter b, offers a theoretical framework to explore packing constraints imposed by molecular interactions. At $n = 1/b$, we observe a vanishing Fano factor ω, signifying suppressed particle number fluctuations. This behavior highlights the reduced configurational complexity due to geometric constraints, with implications for dense granular systems and high-pressure materials design. We use an auxiliary temperature T_w that emerges as a critical diagnostic tool, reflecting the scaling of fluctuations and bridging microscopic interactions with macroscopic stability. In supercritical fluids, we show that the Fano factor provides a sensitive parameter to detect instability thresholds near the spinodal line, revealing the intricate transitions between liquid-like and gas-like states. Our findings underscore the importance of fluctuations in modeling the nuanced thermodynamics of confined fluids and industrial supercritical reservoirs. Our results advance the vdW framework by connecting fundamental thermodynamic principles to actionable insights for practical technologies, particularly in the optimization of supercritical extraction and drying processes. This dual emphasis enhances our understanding of complex systems, marking a meaningful contribution to both theoretical and applied domains. We will see that a putative solid phase is predicted by the van der Waals equation at high densities. Importantly enough, we find that the Fano factor is able to detect the limits of applicability for the van der Waals method.

Keywords: van der Waals (vdW); Fano factor; critical variables; applicability limits for the vdW approach

1. Introduction

Fluctuations are a cornerstone of statistical mechanics, revealing critical information about the microscopic properties of thermodynamic systems. Among various measures of fluctuations, the Fano factor, defined as the ratio of the variance to the mean of a stochastic variable, has emerged as a versatile diagnostic tool. Traditionally employed in contexts such as quantum optics, particle counting, and transport phenomena, the Fano factor quantifies the relative strength of fluctuations and provides insight into the underlying dynamics of the system. This work extends its application to the domain of real gases, specifically the van der Waals gas, to probe the interplay between particle number fluctuations and the equation of state.

The van der Waals equation of state [1–4] is a foundational model in the study of real gases, accounting for intermolecular interactions and the finite size of molecules. While the model provides a robust framework for understanding deviations from ideal gas behavior, the statistical properties of fluctuations, especially in the context of phase transitions and critical phenomena, remain an area of active inquiry. The Fano factor offers a unique lens through which to examine these fluctuations, potentially uncovering signatures of phase coexistence, critical behavior, and regions of thermodynamic instability.

In this paper, we investigate the Fano factor [5,6] for particle number fluctuations in the grand canonical ensemble formulation of the van der Waals gas for two special cases: super dense fluids and super critical ones. By systematically analyzing its behavior across various thermodynamic regimes, we reveal striking phenomena, including the emergence of zeroes and divergences of the Fano factor. These features are shown to correspond to suppressed fluctuations and critical points, respectively, offering a novel perspective on the statistical mechanics of the van der Waals system.

The paper is organized as follows. Sections 2 and 3 remind the reader of the basic elements needed for pursuing our endeavor. Our novelties begin in Section 4, where we tackle the issue of super dense system, while Section 5 is devoted to exploring the van der Waals equation for super critical fluids. A summary in Section 6 closes the article.

2. Our Main Tool: The Fano Factor

The Fano factor [5–7] is a measure used in statistics and various scientific fields to quantify the dispersion of a probability distribution $p(x)$ [5,6]. It was originally introduced to provide foundational insights into the statistical behavior of ionization processes, which has since found applications in various fields. The Fano factor is particularly useful in fields such as physics, neuroscience, and telecommunications to assess the level of fluctuations relative to the average level of a stochastic process. It is defined as the ratio of the variance $\sigma^2 = \langle(\Delta x)^2\rangle$ and the mean $\mu = \langle x \rangle$ of a random process x, which is defined as

$$\mathcal{F} = \frac{\sigma^2}{\mu}. \tag{1}$$

By definition $\mathcal{F} = 1$ for a Poissonian process where the variance equals the mean. If a Poisson distribution is over dispersed relative to another Poisson distribution, it means there are more fluctuations than would be expected in a Poisson process, and $\mathcal{F}$ is greater than 1 (more variability than a Poisson process). Conversely, a Fano factor less than 1 indicates under dispersion, meaning the process has fewer fluctuations than a Poisson process (less variability).

The Fano factor is a useful measure in various fields because it provides insights into the variability and noise characteristics of a system relative to its mean behavior [7–10]. Here are some key reasons why the Fano factor is particularly useful:

1. Since the Fano factor is a dimensionless quantity, it allows for comparison across different systems or data sets that may have different scales or units.
2. This can be particularly useful in neuroscience, for example, where one might want to compare the variability of spike trains between different neurons or brain regions.
3. In fields like physics and electrical engineering, the Fano factor helps in understanding the noise characteristics of a system. It can indicate the presence of correlations or other underlying processes contributing to the observed variability.
4. For instance, in photon counting, a Fano factor different from 1 can reveal information about the underlying physical processes affecting the photon detection.
5. Many natural and manmade processes do not follow Poisson statistics. The Fano factor helps in identifying such deviations, which can be crucial for modeling and understanding complex systems. A Fano factor different from 1 can indicate non Poissonian activity, suggesting more complex underlying dynamics.
6. Researchers can use the Fano factor to validate theoretical models against empirical data. A model that accurately predicts the mean but fails to predict the correct variability (as indicated by the Fano factor) might need refinement.

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7. It provides a straightforward way to test whether observed data fits a specific distribution, helping to refine hypotheses and models.
8. In statistical mechanics, the Fano factor can help analyze fluctuations in systems at equilibrium or in nonequilibrium states. Thermal sources have more fluctuations than a Poisson process, leading to a Fano factor greater than 1, indicating super Poissonian statistics.
9. In quantum mechanics, the Fano factor is used to study particle statistics and can provide insights into the quantum states of particles, such as electrons or photons.
10. **In the present work we will discover that the Fano factor poses strict limits on the applicability of the van der Waals approach.**

In summary, the Fano factor is a versatile and widely applicable measure that helps researchers and practitioners understand and quantify variability in a system relative to its mean. Its dimensionless nature and applicability across different domains make it a valuable tool for both theoretical analysis and practical applications.

2.1. Fano Factor in the Grand Canonical Ensemble (Variables V, T, N)

In the grand canonical ensemble, the number of particles N is not fixed but fluctuates around an average value $\langle N\rangle$ [11]. Fluctuations in the particle number can be quantified by the variance $\langle(\Delta N)^2\rangle = \langle N^2\rangle - \langle N\rangle^2$. The relative mean square fluctuation in the particle density $n = \langle N\rangle/V$ of a given physical system is given by [11]

$$\frac{\langle(\Delta N)^2\rangle}{\langle N\rangle^2} = -\frac{k_B T}{V}\frac{1}{v}\left(\frac{\partial v}{\partial P}\right)_T = \frac{k_B T}{V}\kappa_T, \tag{2}$$

where $v = 1/n$, and

$$\kappa_T = -\frac{1}{v}\left(\frac{\partial v}{\partial P}\right)_T, \tag{3}$$

represents the isothermal compressibility of the system [11].

Consequently, the Fano factor for a physical system in the grand canonical ensemble, which we denote with the letter ω, becomes

$$\omega = \frac{\langle(\Delta N)^2\rangle}{\langle N\rangle} = \frac{k_B T\langle N\rangle}{V}\kappa_T. \tag{4}$$

We see a connection with thermodynamics through the isothermal compressibility. The relation will become relevant in the next Sections.

2.2. Null Fano Factor

A null Fano factor can reveal several important features about a system's behavior, particularly in the context of statistical mechanics and quantum systems. A Fano factor of zero indicates that the variance is zero, meaning there are no fluctuations in the quantity being measured. This situation suggests a highly ordered or deterministic system. In addition:

1. A null Fano factor indicates that the system exhibits no stochastic fluctuations. The quantity measured (e.g., particle number) is constant and perfectly predictable. This is often seen in perfectly ordered or crystalline systems where the arrangement of particles does not vary.
2. In the context of phase transitions, a null Fano factor can indicate a transition to a more ordered phase, such as from a fluid or gas to a solid. This can be particularly insightful in systems undergoing condensation or crystallization, where the particles settle into a fixed, repeating structure.
3. In quantum systems, a null Fano factor can signify a state of perfect quantum coherence. This means that the particles or qubits are in a perfectly correlated state, with no decoherence or random noise affecting their behavior. This is crucial for applications in quantum computing and quantum information where maintaining coherence is essential.

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4. A null Fano factor can also indicate mechanical stability. **We will see below that in the putative solid phase that the van der Waals equation will be seen to predict at high densities**, the absence of fluctuations implies that the system is mechanically stable and resistant to perturbations.

Applications: Understanding the conditions that lead to a null Fano factor can help in the design of materials with specific properties, such as high mechanical stability or low noise in electronic devices. Maintaining a null Fano factor in qubits or other quantum states can enhance the performance of quantum computers by reducing error rates and improving coherence times. Accordingly, in our present study, the Fano factor can be used as a diagnostic tool to understand the nature of different phases and the transitions between them.

The null Fano factor is a significant indicator of various physical phenomena, from deterministic behavior and mechanical stability to quantum coherence and strong interparticle interactions. Identifying and understanding this feature can provide deep insights into the nature of the system under study and has practical implications across multiple fields, including material science, quantum computing, and statistical mechanics.

3. Recalling the vdW Landscape

The van der Waals equation represents a significant advancement in the field of thermodynamics, introducing conspicuous corrections to the ideal gas law to account for the behavior of real gases. Unlike the ideal gas law, which assumes point like particles and no intermolecular forces, the vdW equation incorporates the finite size of molecules and their intermolecular attractions. This inclusion of molecular volume prevents infinite compression, thus implying a form of volume exclusion. Despite these enhancements, the vdW equation has not yet been explicitly associated with the formation of crystalline or maximally dense packing arrangements that are characteristic of solid phases [1,3,4]. This will be done here.

Developed to provide a more accurate description of real gas behavior, the vdW equation has been instrumental in understanding phase transitions and the behavior of gases under various conditions of temperature and pressure. However, there are still intriguing aspects of this equation that invite further exploration. In this study, we investigate the conditions under which the vdW Fano factor vanishes. Our findings reveal that under certain special conditions, this vanishing Fano factor leads to a highly compact system. This observation offers a novel statistical mechanical perspective on the behavior of gases described by the van der Waals equation, suggesting new insights into the dense packing phenomena.

The van der Waals equation can be regarded as a mean-field equation. The mean-field theory simplifies the behavior of a system with many interacting particles by considering the effect of all other particles on any given particle as an average or "mean-field" effect rather than dealing with the complex, many-body interactions directly.

The van der Waals equation is given by:

$$\left(P + \frac{a}{V^2}\right)(V - b) = RT, \tag{5}$$

where $R = k_B N_A$ is the universal gas constant, k_B is the Boltzmann constant, and N_A is the Avogadro constant. This equation introduces two key modifications to the ideal gas law to account for real gas behavior:

1. Finite molecular size (volume exclusion): The parameter b in the equation replaces the volume V by $(V - b)$ and accounts for the finite volume occupied by gas molecules. It effectively reduces the available volume for the gas molecules to move in, reflecting the volume exclusion effect where each molecule has a finite size and thus cannot occupy the same space as another molecule.
2. Intermolecular forces (attractive force of strength a): A term a/V^2 represents the attractive forces between molecules. This term reduces the pressure exerted by the gas molecules on the container

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walls, as these intermolecular attractions pull the molecules inward, making them collide less frequently with the walls.

The term a/V^2 can be seen as the mean field correction for the attractive interactions between molecules. It represents an average effect of all other molecules on a given molecule, rather than detailing specific pairwise interactions. The term $(V - b)$ accounts for the finite size of molecules, effectively modifying the volume available for molecular motion. By incorporating these mean field corrections, the van der Waals equation provides a more accurate description of the behavior of real gases compared to the ideal gas law. It simplifies the complex interactions within the gas to an average effect, consistent with the mean field approach

3.1. Isothermal Compressibility κ_T

Introducing $v = V/\langle N \rangle$, the thermodynamic equation of state for the van der Waals gas in the grand canonical ensemble becomes [12]:

$$P = \frac{k_B T}{v - b} - \frac{a}{v^2}. \tag{6}$$

Therefore, the isothermal compressibility can be calculated from Equation (6) by using Equation (3), which results in the expression

$$\kappa_T = \frac{v^2 (v - b)^2}{k_B T v^3 - 2a(v - b)^2}, \tag{7}$$

or, in terms of the density $n = 1/v$

$$\kappa_T = \frac{(1 - nb)^2}{k_B T n - 2an^2 (1 - nb)^2}, \tag{8}$$

4. Density's Maximum Theoretical Limit

Combining Equations (4) and (8), the Fano factor becomes

$$\omega = \frac{(1 - nb)^2}{1 - (2a/k_B T)\, n\, (1 - nb)^2}. \tag{9}$$

This expression is the one already obtained in Refs. [12,13], but expressed in reduced variables.

By defining now an important auxiliary temperature

$$T_w = (2a/k_B)\, n\, (1 - nb)^2, \tag{10}$$

we can express the Fano factor as follows

$$\omega = \frac{(1 - nb)^2}{1 - T_w/T}. \tag{11}$$

If the parameters of the van der Waals gas are $a = b = 0$, then $T_w = 0$ and $\omega = 1$, which corresponds to the ideal gas case. We see that, when $T > T_w$, the Fano factor $\omega > 0$ (otherwise $T < T_w$ implies $\omega < 0$). The instance $n = 1/b$ that of **maximum possible density (MPD)**. The relationship between particle density n, interactions, and fluctuations is given by the expression (9) above for the Fano factor. Let us look at it from an MPD viewpoint. The MPD $n = 1/b$ instance represents a packing limit where the density is determined solely by the excluded volume per particle, b. At this density, the system is so constrained by the excluded volume effect that further compression of the particles becomes impossible without violating their finite size. At $n = 1/b$, the numerator $(1 - nb)^2 = 0$, driving the Fano factor ω to zero. Physically, $\omega = 0$ signifies the complete suppression of particle number fluctuations. This reflects a regime where the density fluctuations vanish due to the rigid spatial arrangement of particles.

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When $n = 1/b$, the system is essentially incompressible. This marks a thermodynamic limit beyond which no meaningful phase behavior or fluctuation driven phenomena can occur. The vanishing of the Fano factor highlights the dominance of the excluded volume effect, with attractive interactions a playing a secondary role. The auxiliary temperature $T_w = (2a/k_B)n(1 - nb)^2$ encapsulates the effects of attractive interactions a and the density-dependent excluded volume factor. Its appearance in the Fano factor expression:

$$\omega = \frac{(1 - nb)^2}{1 - T_w/T}, \tag{12}$$

serves as a diagnostic for fluctuation behavior across different thermodynamic regimes. *For small densities* ($n \ll 1/b$), T_w *is negligible*, and $\omega \sim (1 - nb)^2$. The Fano factor is driven by volume exclusion and decreases with increasing density. As n increases, T_w becomes significant. If $T_w/T \to 1$, the denominator diverges, and ω increases sharply, signaling critical or unstable thermodynamic conditions. To repeat: at $n = 1/b$, T_w reaches its maximum value, but $(1 - nb)^2 \to 0$, forcing $\omega = 0$. Fluctuations are entirely suppressed due to rigid geometric constraints. Note that T_w is a lowest limit for the temperature, since the Fano factor can no be negative (see next Subsection).

The maximum possible density (MPD), $n = 1/b$, represents a critical density threshold in the van der Waals gas, where fluctuations vanish, and the system becomes incompressible due to finite size effects. The auxiliary temperature T_w provides a useful parameter to study how interactions and density influence fluctuation behavior across different thermodynamic regimes. These findings highlight the intricate interplay of excluded volume, attractive forces, and thermal energy in determining the statistical and thermodynamic properties of the van der Waals gas. The density $n = 1/b$, corresponding to the maximum possible density (MPD) in the context of the van der Waals gas model, is not physically attainable in a real system. Here is why:

The parameter b in the van der Waals equation represents the excluded volume per particle due to their finite size. At $n = 1/b$, the total excluded volume of all particles exactly equals the system's entire volume. This implies a state where particles are packed so tightly that no free volume remains for translational motion. In such a scenario, the particles would effectively overlap, which is physically impossible due to their finite size. The van der Waals equation is a phenomenological model designed to correct the ideal gas law by accounting for finite particle size (excluded volume) and interparticle attractions. However, it assumes that particles remain distinct and do not physically compress into each other. Near $n = 1/b$, the assumptions underlying the van der Waals equation break down: The excluded volume effect $(1 - nb)$ approaches zero, leading to divergences in the pressure and other thermodynamic quantities. The model no longer accurately represents the system's physical behavior at extreme densities.

In real gases or liquids, particles experience quantum mechanical repulsion at very short distances (Pauli exclusion principle for fermions or electron cloud overlap for all atoms). This prevents densities approaching $n = 1/b$. Before $n = 1/b$ is reached, the system will likely undergo a phase transition to a more ordered state, such as: 1) Crystallization into a solid, where particles arrange themselves in a lattice with less compressibility. 2) The onset of new physical phenomena (e.g., quantum effects) if the particles are fermions or bosons.

4.1. Recapitulation

While $n = 1/b$ can be treated mathematically as a limiting case in the van der Waals equation, it serves more as a conceptual boundary than a physically realizable state. The divergence of the Fano factor ω and other quantities as $n \to 1/b$ indicates that the model loses predictive power in this regime.

The density $n = 1/b$ represents a theoretical limit rather than a physically realizable state. It highlights the geometric constraint imposed by the finite size of particles and marks the point where the van der Waals model ceases to apply. In real systems, the actual density will always be less than $1/b$, with particles either

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crystallizing, experiencing strong repulsive forces, or transitioning to another phase well before this limit is reached.

4.2. Limits on the Applicability of the vdW Approach

At the risk of some redundancy and revisiting Equation (12), let us emphasize the fact that a negative Fano parameter indicates the breakdown of the van der Waals model at temperatures below T_w. This implies:

- The van der Waals temperature cannot become arbitrarily small.
- The model is not valid below T_w, and the system transitions to a regime where the assumptions of the van der Waals equation no longer hold.

Determining T_w, as we have done here, provides important insight into the limitations of the model and highlights the onset of new physics, such as phase transitions or quantum effects, that require more advanced treatments.

5. Fano Factor and Supercritical Fluids

As we all know, supercritical fluids [14] exist above the critical temperature T_c and critical pressure P_c, where traditional distinctions between liquid and gas phases no longer exist. In this regime, a so called Widom line [15] divides regions with liquid-like properties (higher density and stronger molecular interactions) from those with gas-like properties (lower density and weaker interactions).

Studying supercritical fluids (SCFs) is of great interest due to their unique thermo-physical properties and their broad applications in science and technology. Unlike classical fluids, SCFs exhibit unusual transport properties, compressibility, and heat capacity anomalies, making them interesting for fundamental studies. Supercritical fluids represent an interdisciplinary research area, connecting statistical mechanics, thermodynamics, chemistry, astrophysics, and engineering. Their properties make them highly relevant for both theoretical studies and real-world applications [14].

Supercritical fluids occur due to classical thermodynamic effects, where thermal fluctuations prevent phase separation. Example: carbon dioxide ($CO2$) becomes a supercritical fluid above its critical temperature (31 $\circ C$) and critical pressure (73 atm). Its key property is a hybrid behavior: it can diffuse like a gas but dissolve substances like a liquid.

Supercriticality is NOT an exotic issue. 1) Supercritical $CO2$ is used in a) decaffeinating coffee, b) essential oil extraction, and c) purifying pharmaceuticals. 2) Supercritical Water Oxidation is used for waste treatment due to its ability to dissolve and react with organic matter efficiently. 3) Supercritical chromatography provides a faster and greener alternative to high-performance liquid chromatography. 4) Significant parts of the Jupiter and Saturn atmospheres are supercritical.

5.1. Widom Line

The Widom line [15] is a concept used in the study of supercritical fluids and phase transitions. It is defined as the locus of maxima in certain thermodynamic response functions, such as heat capacity, compressibility, or thermal expansion coefficient, above the critical point of a fluid. The Widom line serves as a continuation of the liquid-gas coexistence curve into the supercritical region, marking a crossover between liquid-like and gas-like behaviors. Let us single out its key features:

1. Below the critical point, phase transitions occur as distinct boundaries between phases. Above the critical point, the Widom line represents a gradual, continuous crossover instead of a sharp phase change.
2. Along the Widom line, the correlation length and other thermodynamic properties show maxima, reflecting remnants of critical behavior.
3. It helps to identify regions where the properties of the supercritical fluid behave more like a liquid or a gas, which is useful for applications in chemical engineering, material science, and thermodynamics.

We can construct the Widom line using thermodynamic response functions. For instance:

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1. In temperature-pressure (TP) space, it is the line along which the isobaric heat capacity C_P reaches its maximum.
2. In density-temperature (nT) space, it marks the crossover between liquid-like and gas-like regions.

Summing up, the Widom line is the locus of points in the supercritical region where an appropriate thermodynamic response functions (e.g., heat capacity, compressibility, or thermal expansion coefficient) reach their maximum values. It is often associated with the remnants of the liquid-gas coexistence line, continuing as a "crossover" line in the supercritical fluid regime. Let us insist: along the Widom line, thermodynamic properties exhibit maxima, reflecting the persistence of liquid-like and gas-like behaviors. For example:

1. Heat capacity peaks as the system transitions between liquid-like and gas-like states.
2. Compressibility also peaks, indicating a crossover in the molecular structure.

These maxima become less pronounced as the system moves farther from the critical point.

5.2. Characteristics of a Supercritical Fluid

The study of supercritical fluids [14] within the van der Waals framework reveals unique insights into the fluctuation driven behavior of systems beyond the critical point. These findings underscore the relevance of the Fano factor and its divergence at the spinodal line (see below) as a diagnostic tool for analyzing supercritical phenomena.

It is our turn now to recall that the so called spinodal line is also a critical concept in thermodynamics and phase transitions, representing the limit of local stability for a system. It is a boundary within the phase diagram of a substance that separates regions of stability from regions where the system becomes unstable with respect to small fluctuations. The spinodal line is defined as the locus of points in a phase diagram where the second derivative of the free energy with respect to density (or another order parameter) becomes zero. This condition implies that the thermodynamic stability criteria are violated, making the system unstable under small perturbations.

To repeat again then, a supercritical fluid is a state of matter that occurs when a substance is at a temperature and pressure above its critical point. In this state, the fluid exhibits properties that are intermediate between those of a liquid and a gas, blending characteristics of both phases. We have seen that the critical point is defined by a specific temperature T_c and pressure P_c at which the distinction between the liquid and gas phases disappears. At this point the liquid and gas phases have the same density. Also, surface tension vanishes, so the fluid no longer has a well defined interface between phases. Characteristics of a supercritical fluid are stated below:

1. A supercritical fluid possesses unique properties due to its hybrid nature. Its density is similar to that of a liquid, enabling it to dissolve substances effectively.
2. Its viscosity is similar to that of a gas, allowing it to flow easily and penetrate porous materials.
3. It is highly compressible, like a gas, making its density tunable by changing pressure or temperature.
4. Its diffusivity is intermediate between those of liquids and gases, allowing relatively fast molecular diffusion compared to liquids.

On a pressure-temperature $(P-T)$ phase diagram, the critical point lies at the end of the liquid-gas coexistence curve (binodal curve). Beyond this point $(T > T_c, P > P_c)$, the substance is in the supercritical fluid region, where no distinct liquid or gas phase exists.

We mention as an example of supercritical fluids the case of carbon dioxide (CO_2), a common supercritical fluid used in decaffeinating coffee, extracting essential oils, and as a solvent in green chemistry. Supercritical water is used in power plants, chemical synthesis, and as a medium for waste decomposition.

The behavior of a supercritical fluid can be further modified by adjusting its temperature and pressure. Near the critical point, the fluid is highly compressible, and small changes in pressure or

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temperature cause large changes in density. Far from the critical point, it behaves more uniformly, with properties stabilizing between those of a liquid and gas.

Supercritical fluids challenge the traditional understanding of matter as distinctly liquid, gas, or solid. Their hybrid nature not only provides a unique perspective on phase transitions but also offers a versatile platform for technological innovation and scientific exploration.

For our purposes it is significant that super critical fluids are characterized by the large inhomogeneity of molecular distributions. The density fluctuation becomes for them a suitable parameter for a quantitative and direct description of inhomogeneity from the viewpoint of mesoscopic or macroscopic scales.

The gas-liquid coexistence curve (binodal) marks the boundary where gas and liquid phases are in thermodynamic equilibrium. On either side of this curve, a single phase (gas or liquid) is thermodynamically stable. The spinodal curve lies within the coexistence region and indicates the boundary of local stability for the gas or liquid phase. Beyond the spinodal curve, a phase becomes thermodynamically unstable, and small fluctuations spontaneously grow, driving the system toward a different phase.

5.3. Our vdW Treatment in Terms of Critical Variables

Recall that the Fano factor measures the ratio of variance σ^2 to the mean $\langle N \rangle$ of particle number fluctuations. It reflects the relative strength of fluctuations in a system. As the system approaches the spinodal curve: i) The thermodynamic susceptibility (e.g., isothermal compressibility, κ_T diverges), ii) Large fluctuations dominate, because the system becomes increasingly unstable to density perturbations, and iii) This divergence in fluctuations translates directly into a divergence of the Fano factor

$$w = \frac{\sigma^2}{\langle N \rangle} \propto \kappa_T.$$

The critical temperature, pressure, and volume of a gas are, respectively, 1) Critical temperature T_c: The highest temperature at which a gas can change into a liquid. It's a measure of the force of attraction between the molecules, 2) Critical pressure P_c: The pressure required to liquefy a gas at its critical temperature. Critical volume v_c: The volume of one mole of a gas that has been liquefied at its critical temperature. These three quantities define the so called critical point.

At the critical point (P_c, v_c, T_c), the isotherm in the PV phase diagram has a point of inflection [4]:

$$\left(\frac{\partial P}{\partial v}\right)_{T=T_c} = 0 \quad \text{and} \quad \left(\frac{\partial^2 P}{\partial v^2}\right)_{T=T_c} = 0. \tag{13}$$

Using these conditions, *the following van der Waals critical parameters can be derived*:

$$v_c = 3b, \quad T_c = \frac{8a}{27k_B b}, \quad P_c = \frac{a}{27b^2}. \tag{14}$$

Reduced variables are defined as $\widetilde{P} = P/P_c, \widetilde{v} = v/v_c$, and $\widetilde{T} = T/T_c$. In terms of them the van der Waals Equation (6) becomes

$$\widetilde{P} = \frac{8\widetilde{T}}{3\widetilde{v} - 1} - \frac{3}{\widetilde{v}^2}, \tag{15}$$

which can also be written in terms of the reduced density $\widetilde{n} = n/n_c$

$$\widetilde{P} = \frac{8\widetilde{T}\widetilde{n}}{3 - \widetilde{n}} - 3\widetilde{n}^2, \tag{16}$$

where $n_c = 1/v_c = 1/3b$ is the critical density.

Similarly, the Fano factor is rewritten as follows [16]:

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$$\widetilde{w} = \frac{1}{9}\frac{(3-\widetilde{n})^2}{1-\frac{\widetilde{n}(3-\widetilde{n})^2}{4\widetilde{T}}}, \tag{17}$$

while the auxiliary temperature T_w (10) in reduced variables is written as

$$\widetilde{T}_w = \frac{T_w}{T_c} = \frac{\widetilde{n}(3-\widetilde{n})^2}{4}. \tag{18}$$

Notice that the reduced Fano factor $\widetilde{w}$ (Equation (17)) diverges at the low temperature such that $\widetilde{T} = \widetilde{T}_w$, with $\widetilde{T}_w$ given by Equation (18). **This is a notable Fano feature**.

Near the spinodal curve, the restoring forces that maintain the local stability of the phase become weak. Small fluctuations in density or particle number grow unchecked. The system becomes increasingly "soft", with correlations extending over long distances (critical slowing down), which amplifies the variance of fluctuations.

Let us repeat that the spinodal curve represents the limit where local stability is lost. Here, any perturbation, no matter how small, leads to a complete phase separation. The Fano factor diverges because the variance of fluctuations becomes infinitely large, while the mean remains finite, reflecting the catastrophic breakdown of the phase.

Implications: The divergence of the Fano factor at the spinodal line provides:

1. A theoretical signature of the spinodal limit in the van der Waals gas or similar systems.
2. A practical diagnostic for identifying instability thresholds in real gases or fluids, where direct measurements of fluctuations can reveal the spinodal behavior, and
3. insight into the relationship between fluctuations, phase stability, and susceptibility in complex systems.

The divergence of the Fano factor along the gas-liquid spinodal curve is a striking manifestation of the fundamental connection between fluctuations and phase stability. It underscores the power of fluctuation based metrics, like the Fano factor, to probe critical and precritical phenomena in thermodynamic systems. This behavior not only deepens our understanding of phase transitions but also has potential applications in experimental studies of real gases and fluids.

5.4. Other Features

It is quite interesting to note that the line depicting the behavior of the auxiliary temperature $\widetilde{T}_w$ coincides with the spinodal line (or gas-liquid coexistence curve) given by Equation (16) in Ref. [16], which is the locus of the extrema of the isotherms. This is obtained from $(\partial\widetilde{P}/\partial\widetilde{n})_{\widetilde{T}=\widetilde{T}_w} = 0$. **Along this spinodal curve, the reduced Fano factor diverges**.

Define the temperature $\widetilde{T}_u$ as the temperature at which the following derivative vanishes

$$\left(\frac{\partial\widetilde{w}}{\partial\widetilde{n}}\right)_{\widetilde{T}=\widetilde{T}_u} = 0. \tag{19}$$

This vanishing feature has links with the Widom line [17]. Thus, there is some connection between the Widom line and

$$\widetilde{T}_u = \frac{(3-\widetilde{n})^3}{8}. \tag{20}$$

This is to be compared to Equation (17) of Ref. [16]. This equation corresponds to the locus of the inflection point determined by the condition $(\partial^2\widetilde{P}/\partial\widetilde{n}^2)_{\widetilde{T}=\widetilde{T}_u} = 0$. Let us discuss this relation in more detail. F

The temperature $\widetilde{T}_u = (3-\widetilde{n})^3/8$, derived as the condition where the Fano factor's density derivative vanishes, if adequately plotted exhibits interesting features that align conceptually with properties of the Widom line. However, it is not the same as the Widom line but can be interpreted as a related characteristic curve.

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Key properties of $\widetilde{T}_u$ are:

1. Decreasing $\widetilde{T}_u$ with increasing $\widetilde{n}$. As density increases and $\widetilde{n}$ approaches 3, the characteristic temperature $\widetilde{T}_u$ decreases. This aligns with the expectation that fluctuation extrema (as captured by the Fano factor) shift to lower temperatures in denser regimes where repulsive interactions (excluded volume effects) dominate.
2. $\widetilde{T}_u = 0$ at $\widetilde{n} = 3$. At $\widetilde{n} = 3$, the density reaches its limiting value, which corresponds to the maximum packing condition $n = 1/b$ in dimensional terms. Here, $(3 - \widetilde{n})^3 = 0$ suppresses $\widetilde{T}_u$, indicating that fluctuations are completely constrained by the repulsive interaction.
3. Nonlinear Cubic Dependence. The $(3 - \widetilde{n})^3$ term reflects a strong nonlinear interplay between attractive a and repulsive b interactions, scaling the temperature nonlinearly as the system approaches critical or high density states. This scaling encapsulates the combined. Effect of thermodynamic quantities, resembling the behavior of thermodynamic response functions near phase transition regions.

Relation of $\widetilde{T}_u$ to the Widom Line: The Widom line marks the locus of maxima of thermodynamic response functions (e.g., heat capacity, compressibility) and serves as a signature of the crossover between liquid-like and gas-like behaviors in the supercritical regime. While $\widetilde{T}_u$ is derived from fluctuation's behavior, it shares certain conceptual similarities with the Widom line. These are:

1. Fluctuation Extremes: The Widom line corresponds to maxima in fluctuation driven response functions. Similarly, $\widetilde{T}_u$ represents a condition tied to the behavior of fluctuations, specifically where the density derivative of the Fano factor $\widetilde{w}$ vanishes, indicating a transition in fluctuation behavior.
2. Supercritical Implications: Although the Widom line typically lies in the supercritical region, $\widetilde{T}_u$ could extend into the subcritical region, suggesting a possible crossover like behavior that includes critical phenomena.
3. Temperature-Density Relationship: The cubic dependence of $\widetilde{T}_u$ on $(3 - \widetilde{n})$ reflects scaling that could be interpreted as a remnant of critical scaling laws, which are central to Widom line phenomena.

Limitations of Identifying $\widetilde{T}_u$ as the Widom line: The Widom line is typically associated with the supercritical phase, while $\widetilde{T}_u$ is derived from fluctuation behavior and could apply to both subcritical and supercritical regimes. The Widom line's definition relies on the behavior of macroscopic response functions, such as heat capacity or compressibility, whereas $\widetilde{T}_u$ emerges from microscopic fluctuation analysis (the Fano factor).

While $\widetilde{T}_u$ does not strictly represent the Widom line, it shares similar themes: a) Both characterize transitions in fluctuation behavior. b) Both reflect the interplay of attractive and repulsive forces. c) Both have temperature-density relationships influenced by critical phenomena.

Thus, $\widetilde{T}_u$ could be considered a fluctuation specific analog to the Widom line, offering complementary insight into the system's behavior, particularly in regimes influenced by excluded volume effects and fluctuation extremes.

6. Conclusions

Our primary goal here was to present new insights into the van der Waals model fluctuations, focusing on: 1) the concept of maximum possible density (MPD) on the one hand and 2) Fano applications to supercritical fluids on the other. Our effort should interest physicists, chemists and engineers interested in statistical mechanics, thermodynamic modeling, and supercritical fluid applications. Accordingly, our work examined the two interrelated aspects of the van der Waals (vdW) equation outlined above: 1) the concept of maximum possible density (MPD), $n = 1/b$, and 2) the application of the vdW model to understanding supercritical fluids. **Also, an analysis of the pertinent Fano factor discovered strict limits on the applicability of the vdW methodology**. We believe that these investi-

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gations contribute valuable insights into the complexity of statistical and thermodynamic behavior in systems exhibiting critical and near-critical phenomena.

6.1. *Van der Waals Maximum Possible Density (MPD)*

Our present MPD instance, $n = 1/b$, refers to a theoretical packing limit based on the vdW excluded volume parameter b, which accounts for the finite size of particles. This concept highlights the complex interplay between geometric constraints and molecular interactions, offering an understanding of how packing limits govern dense system behavior. We found that

As insight into Fluctuation Behavior: We saw that for $n = 1/b$, the Fano factor ω vanishes, signifying suppressed particle number fluctuations due to rigid spatial arrangements. This phenomenon illustrated that the reduction in system complexity, as fluctuations and configurational freedom, are constrained by geometry.

A diagnostic role of our auxiliary temperature T_w: The auxiliary temperature T_w encapsulates attractive interactions a and density-dependent volume exclusion, providing a bridge between microscopic interactions and macroscopic thermodynamic stability. The dependence of T_w on density and temperature reflects the complex scaling behavior of fluctuations across regimes.

These findings have practical applications in materials science, where understanding packing limits and fluctuation suppression is critical for designing dense granular systems or high pressure processes. The MPD also provides a framework for probing the emergent complexity in dense systems, such as colloids and granular materials.

6.2. *Supercritical Fluids*

Our present vdW equation's application to supercritical fluids provided valuable insights into the complex nature of systems where traditional phase transitions give way to continuous crossovers.

We saw that the Fano factor ω serves as a sensitive parameter for detecting instability thresholds near the spinodal line. This diagnostic capability highlights the emergent complexity of supercritical regimes, where fluctuations reveal nuanced transitions between liquid-like and gas-like behavior.

We emphasize that supercritical fluids are essential in industries such as food processing and pharmaceuticals. Understanding their complex thermodynamic behavior, particularly fluctuations and stability, is vital for optimizing processes like supercritical extraction and drying.

The divergence of ω near the spinodal line links density fluctuations, phase stability, and thermodynamic susceptibility. These relationships provide a foundation for modeling the multifaceted behavior of confined fluids and natural or industrial supercritical reservoirs.

In summary, our present research advances the theoretical framework of the van der Waals equation while offering actionable insights for understanding and manipulating complex thermodynamic systems. This dual focus makes the work a meaningful contribution to both fundamental science and applied technologies.

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