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Mechanical Instabilities and the Mathematical Behavior of van der Waals Gases

Flavia Pennini [1,2] and Angelo Plastino [3,*]

[1] Departamento de Física, Universidad Católica del Norte, Av. Angamos 0610, Antofagasta 1270709, Chile; fpennini@ucn.cl
[2] Departamento de Física, Facultad de Ingenieria, Universidad Nacional de Mar del Plata (UNMDP), CONICET, Av. J.B. Justo 4302, Mar del Plata CP 7600, Argentina
[3] Instituto de Física La Plata—CCT-CONICET, Universidad Nacional de La Plata, C.C. 727, La Plata 1900, Argentina
* Correspondence: plastino@fisica.unlp.edu.ar

Abstract: We explore the mathematical behavior of van der Waals gases at temperatures where classical descriptions are inadequate due to emerging quantum effects. Specifically, we focus on temperatures T_2 at which the thermal de Broglie wavelength becomes comparable to the interparticle spacing, signifying the onset of quantum mechanical influences. At such temperatures, we find that the isothermal compressibility of the gas becomes negative, indicating mechanical instability. In the pressure–density diagrams, we note that the pressure can become negative at small densities, illustrating the limitations of classical models and the necessity for quantum mechanical approaches. These phenomena serve as clear indicators of the transition from classical thermodynamics to quantum statistical mechanics. The observed mechanical instability and negative pressures represent rare macroscopic manifestations of quantum effects, demonstrating their profound impact on gas behavior. Our study highlights the significant role of emerging quantum properties on observable macroscopic scales, particularly for van der Waals gases at low temperatures and small densities. Additionally, we discuss the theoretical implications of our findings, underlining the limitations of the van der Waals model under extreme conditions and emphasizing the critical need to include quantum corrections in thermodynamic frameworks.

Keywords: van der Waals gas; mechanical instabilities; quantum influences

MSC: 82-02; 62E10; 60A10

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1. Introduction

The study of the mathematical behavior of gas models has traditionally been grounded in classical physics, where coherent frameworks and models, such as the ideal gas law, have effectively characterized gas behavior across a wide range of conditions. However, at low temperatures and small interparticle distances, the assumptions underlying classical models become increasingly insufficient as quantum mechanical effects begin to manifest. In particular, van der Waals gases, which account for the finite size of molecules and interactions between them, present interesting challenges at the intersection of classical thermodynamics and quantum mechanics [1].

As the thermal de Broglie wavelength approaches the interparticle spacing, significant quantum effects emerge, fundamentally altering the behavior of these systems [2,3]. At characteristic temperatures, denoted by T_2, where these effects become significant, notable deviations from classical predictions occur [4]. Specifically, our focus here is on how isothermal compressibility behaves under these conditions, revealing that it can transition to negative values, thus indicating mechanical instability.

Negative compressibility is a striking phenomenon that signals the limitations of classical models, suggesting that the gas may be in a non-physical or metastable state. This behavior manifests in pressure–density diagrams, where we observe that pressure can also become negative at low densities. Such findings challenge our understanding of gaseous behavior and underscore the necessity of incorporating quantum mechanics' notions into the mathematical frameworks.

This study aims to bridge the gap between classical thermodynamic model dependencies and the realities presented by quantum statistical mechanics. By meticulously investigating the properties of van der Waals gases at temperatures T_2, we aim to elucidate the significant role of quantum effects in influencing macroscopic properties. We demonstrate that negative pressures and mechanical instabilities serve as clear indicators of the transition from classical to quantum behavior, providing a rare glimpse into the collective phenomena that are typically overlooked in classical frameworks.

This article is organized as follows: Section 2 reviews preliminary materials concerning the van der Waals equation, relevant properties, and discussions about the classical–quantum transition. Section 3 presents various findings. Section 4 contains a physical interpretation using the phase diagram. Section 5 explains the limitations of classical gas models and Section 6 concludes with a summary of the results.

2. Preliminaries

2.1. Van der Waals Equation

One known form of the van der Waals equation of state is given by [4–8]

$$\left(P+\frac{a'}{V_m^2}\right)(V_m-b')=RT, \tag{1}$$

where P is the pressure, V_m is the molar volume, T is the temperature, and $R=N_Ak_B$ is the gas constant, defined as the Avogadro constant N_A multiplied by the Boltzmann constant k_B. Indeed, the quantities $a=a'/N_A^2$ and $b=b'/N_A$ are the van der Waals constants [9]. This equation can be deduced from the grand partition function in the grand canonical ensemble. The next section contains some mathematical tricks.

2.2. Thermal Quantifiers

We are concerned with thermal quantifiers. For starters, the grand canonical partition function is given by

$$Z=\exp\left(\frac{zV}{\lambda^3}e^{-B_2(T)/v}\right), \tag{2}$$

where λ is the average de Broglie thermal wavelength,

$$\lambda=\left(\frac{2\pi\hbar^2}{mk_BT}\right)^{1/2}, \tag{3}$$

where $z=\exp(\mu/k_BT)$ is called the fugacity, μ is the chemical potential, and $v=V/N=V_m/N_A$ is the volume per particle [9–11]. Also, the second virial coefficient $B_2(T)$ describes the contribution of the pairwise potential to the pressure of the gas. It is well known that, for classicality to prevail, the length λ should be much smaller than the average interparticle distance [3,4,10].

The Helmholtz free energy F is [10]

$$F=-k_BT\ln\left[\frac{1}{N!}\left(\frac{V}{\lambda^3}\right)^N\exp\left(-\frac{NB_2(T)}{v}\right)\right], \tag{4}$$

which, by using Stirling's approximation and noting that $B_2=b-a/k_BT$, becomes

$$F = -Nk_BT\left[1 + \ln\left(\frac{v}{\lambda^3}\right)\right] + \frac{Nk_BT}{v}\left(b - \frac{a}{k_BT}\right). \tag{5}$$

Following the textbook recipes [10], from the relation

$$N = z\left(\frac{\partial \ln Z}{\partial z}\right)_{V,T}, \tag{6}$$

we are easily led to the chemical potential of the form

$$\mu = k_BT \ln\left[\frac{\lambda^3}{v} \exp\left(\frac{B_2(T)}{v}\right)\right]. \tag{7}$$

Furthermore, the pressure is

$$P = -\frac{1}{N}\left(\frac{\partial F}{\partial v}\right)_{T,N}, \tag{8}$$

so that we obtain [3,4,10]

$$P = \frac{k_BT}{v}\left(1 + \frac{b}{v}\right) - \frac{a}{v^2}. \tag{9}$$

At a low density, $v \gg b$, one obtains the celebrated van der Waals equation for a dilute gas as [10]

$$P = \frac{k_BT}{v - b} - \frac{a}{v^2}. \tag{10}$$

The above equation is the one that will be used below as the vdW equation.

2.3. Comment on Small Densities

Note that the possible expectation that a higher density could lead to stronger quantum effects in gases is incorrect due to the relationship between quantum effects and the overlap of wave functions in many-particle systems. We explain why.

1. Quantum Effects and the De Broglie Wavelength: Quantum effects in gases become significant when the thermal de Broglie wavelength λ_{dB} of the particles, which represents the spatial extent of a particle's quantum wave packet, becomes comparable to the average distance between particles. The de Broglie wavelength (dBWL) is inversely proportional to the particle's momentum.

At low temperatures, particles have lower momentum, so the dBWL increases, leading to more significant quantum effects as the wave packets of different particles begin to overlap.

2. The Role of Density: Naively, one might think that increasing the density of the gas would push particles closer together, making quantum effects more prominent due to greater wave function overlap. However, this overlooks the following key factor.

The Pauli Exclusion Principle for Fermions: For fermions (particles with half-integer spin, like electrons), the Pauli exclusion principle restricts particles from occupying the same quantum state. At higher densities, fermions "fill up" available quantum states, causing the system to behave more like a degenerate Fermi gas, where the effects are more classical (due to higher energy levels being occupied) unless the temperature is extremely low. Thus, quantum effects, such as Bose–Einstein condensation in bosons or fermionic degeneracy in fermions, only become prominent when densities are low enough for quantum states to overlap [12].

3. Thermal De Broglie Wavelength and Density Relation: At higher densities, the interparticle distance decreases. However, if the temperature remains high, the de Broglie wavelength is still small relative to the distance between particles. Quantum effects only manifest when the thermal de Broglie wavelength is comparable to or larger than the average distance between particles. Increasing the density without reducing the temperature keeps the de Broglie wavelength small, so quantum effects are still suppressed.

In contrast, at low densities and low temperatures, the de Broglie wavelength becomes larger than the average interparticle distance, leading to a significant overlap of quantum wave functions and the emergence of quantum effects like Bose–Einstein condensation or fermionic degeneracy [12].

Summing up, the expectation that a higher density enhances quantum effects is incorrect because quantum effects depend on the ratio of the thermal de Broglie wavelength to the interparticle distance. At higher densities, classical effects dominate unless the temperature is extremely low, as the wave functions cannot overlap significantly without a sufficiently large de Broglie wavelength, which is more easily achieved at low temperatures and low densities.

2.4. Critical Points

The critical points of the van der Waals equation arise because the critical isotherm in a $P - V$ diagram has a point of inflection [11], so

$$\left(\frac{\partial P}{\partial v}\right)_T = 0, \quad \left(\frac{\partial^2 P}{\partial v^2}\right)_T = 0. \tag{11}$$

Solving for them yields the critical values [1,11]:

$$P_c = \frac{a}{27b^2}, \quad v_c = 3b, \quad T_c = \frac{8a}{27k_B b}. \tag{12}$$

2.5. Isothermal Compressibility

The compressibility of a gas is a measure of how much the volume of the gas decreases under pressure. Isothermal compressibility κ_T is defined as

$$\kappa_T = -\frac{1}{v}\left(\frac{\partial v}{\partial P}\right)_T, \tag{13}$$

which, in view of the van der Waals equation of state, i.e., Equation (10), becomes

$$\kappa_T = \frac{v^2(v-b)^2}{k_B T v^3 - 2a(v-b)^2}. \tag{14}$$

Note that κ_T can exhibit peculiar behavior, especially near phase transitions [9]. For a physically stable system, κ_T should be positive because positive compressibility indicates that the volume decreases as pressure increases, which is the expected response of a stable system to compression. If the isothermal compressibility κ_T for a van der Waals gas is negative at low densities and suddenly becomes positive at higher densities, this unusual behavior can be interpreted in terms of stability and the nature of phase transitions in the gas [3,4,9].

2.6. Negative Isothermal Compressibility

When κ_T is negative, it implies

$$\left(\frac{\partial v}{\partial P}\right)_T > 0. \tag{15}$$

This means that an increase in pressure leads to an increase in volume, which is a sign of mechanical instability. Such behavior is non-physical for a stable, homogeneous phase of matter. At low densities, where κ_T is negative, the system may be in a metastable state. This implies that small perturbations can cause the system to move toward a more stable state.

2.7. van der Waals-Associated Classical–Quantum Frontier

The internal energy U for the vdW gas reads as

$$U = F + TS = \frac{3}{2} N k_B T - \frac{Na}{v}, \tag{16}$$

where $S = N k_B \Big(\ln[e^{5/2}(v/\lambda^3)] - (b/v) \Big)$ is the entropy [11]. We follow Ref. [3] here and define $\varepsilon = U/N$ as the energy per particle of the vdW gas and μ as the chemical potential. Accordingly, the central idea for determining the vdW classical regime is the inequality [3,4]

$$\exp(\beta\mu) \ll \exp(\beta\varepsilon). \tag{17}$$

Also (see, once again, [3,4]), the classical regime is characterized by [9]

$$\left(\frac{\lambda^3}{v}\right) \exp\left(\frac{B_2(T)}{v}\right) \ll \exp(\beta U), \tag{18}$$

where B_2 is the second virial coefficient (employed to deduce the vdW equation from the so-called virial expansion [10]), and thus, the de Broglie length should be small enough, as determined by the relation [3,4,10]

$$\frac{\lambda^3}{v} \ll \exp\left(\frac{3}{2} - \frac{b}{v}\right). \tag{19}$$

In Refs. [3,4], the authors introduced the special, all-important indicative temperatures T_2 that signal the classic–quantum passage. The classical regime is obtained at temperatures $T \gg T_2$ such that [3,4]

$$T_2 = \frac{2\pi\hbar^2}{m\, k_B\, e\, v^{2/3}} \exp\left(\frac{2b}{3v}\right), \tag{20}$$

or, in terms of the density $n = 1/v$, the set of our special temperatures becomes determined by

$$T_2 = \frac{2\pi\hbar^2 n^{2/3}}{m\, k_B\, e} \exp\left(\frac{2nb}{3}\right). \tag{21}$$

In Figure 1, we show the behavior of the temperatures T_2 as a function of the density n/N_A for several noble gases. Since the mean interparticle distance (ITD) decreases as the density increases, it takes smaller values of the de Broglie length (DBL) to become larger than the ITD. Since the DBL is inversely proportional to $\sqrt{T}$, T_2 increases with density.

Table 1 lists the van der Waals constants a and b and the masses of the noble gases. Additionally, Table 2 lists, from left to right, the quantum–classical transition temperatures T_2 and the liquid–gas transition temperatures T_c for five noble gases. We observe that the temperatures T_2 are smaller than the critical temperatures T_c.

Table 1. Data on the noble gases. Experimental data for the van der Waals parameters a and b in the International System of Units (SI) are obtained from Ref. [13]. Also, see the table given in Ref. [5].

Gas Name	**a (J m^3/mol^2)**	**b (10^{-3} m^3/mol)**	**m (10^{-3} Kg/mol)**
Helium	0.003460	0.02373	4.0026
Neon	0.02155	0.01626	20.1797
Argon	0.1362	0.03220	39.948
Krypton	0.2316	0.03940	83.798
Xenon	0.4190	0.05154	131.293

Table 2. The classical–quantum transition temperatures T_2 for noble gases are listed in the first column (left). The critical gas–liquid temperatures T_c are shown in the right column. The table considers $n/N_A = 20{,}000$. The data used are in Table 1.

Gas Name	T_2 (°K)	T_c (°K)
Helium	2.02	5.19
Neon	0.37	44.49
Argon	0.23	150.70
Krypton	0.12	209.52
Xenon	0.09	289.73

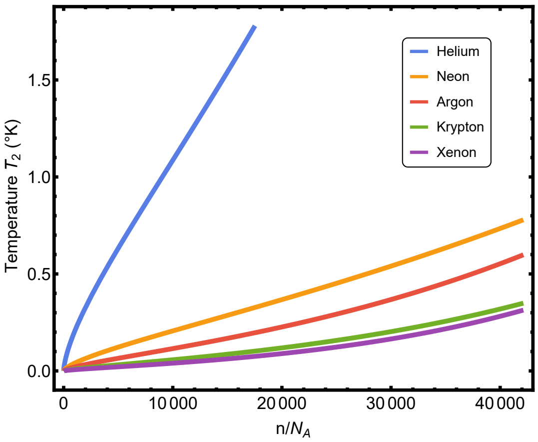

Figure 1. Temperature T_2 versus n/N_A for noble gases. The data used are listed in Table 1, obtained from Ref. [13].

3. Macroscopic Observables Signal the Classic–Quantum Transition

3.1. P-versus-V and P-versus-Density Graphs for Helium

Next, we present a vdW graph of the pressure given by Equation (1) versus volume for Helium gas in Figure 2, providing a visual representation of the relationship between the pressure P and volume V of a noble gas. This type of graph is essential for understanding and analyzing the behavior of gases under different conditions [10].

In the context of a van der Waals (vdW) gas, the behavior of isotherms in a $P - V$ graph during different transitions offers insight into the physical phenomena occurring at specific temperatures. Note that the critical temperature T_c is the *highest temperature* at which a liquid and its vapor can coexist. Above this temperature, there is no distinct phase transition between the liquid and gas phases. At T_c, the isotherm in a $P - V$ graph shows an inflection point where the curve flattens out but does not exhibit a distinct phase transition. The pressure remains positive, and there is no region where P becomes zero or negative. Below T_c, as shown by the orange curve, isotherms display negative pressures, indicating metastable states.

At T_2, we encounter a regime where quantum effects become significant, typically at very low temperatures. In this context, classical gas behavior transitions to quantum gas behavior. The T_2 isotherms exhibit regions where the pressure P becomes negative at very small volumes. This unphysical prediction arises because the classical van der Waals equation does not account for quantum mechanical effects, leading to inaccuracies at low temperatures. In reality, pressure cannot be negative, suggesting that either the attractive forces are overestimated or that the model does not adequately describe the behavior of the gas under these conditions. Similar comments can be made for Figure 3, which depicts pressure versus inverse density $v = V/N$.

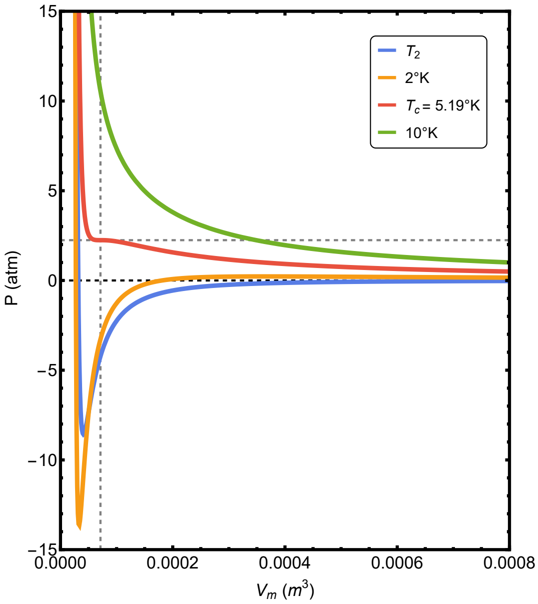

Figure 2. Pressure P versus molar volume V_m for several temperatures. The gray dashed line indicates the critical values of the critical isotherm T_c: $P_c = 2.24$ atm and $V_{m_c} = 0.000071$ m^3. The data used correspond to Helium, as given in Table 1.

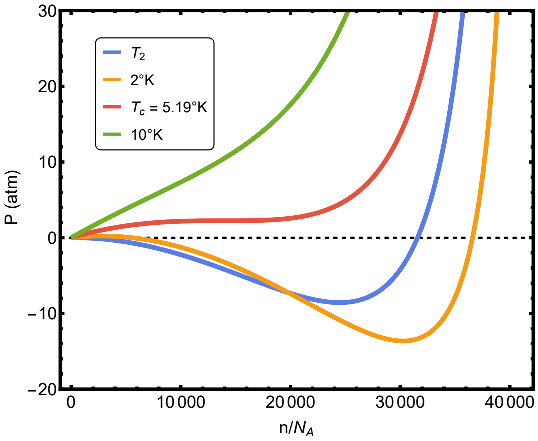

Figure 3. Pressure P versus n/N_A for several temperatures. The data used correspond to Helium, as given in Table 1.

3.2. Isothermal Compressibility

In Figure 4, we depict the behavior of isothermal compressibility versus density. We observe in Figure 4 that, as expected, phase transitions emerge for the van der Waals gas at critical temperatures when plotting the isothermal compressibility against the gas density [11]. One of these transitions is the classic–quantum one around which our present discussion revolves.

The isothermal compressibility κ_T, given by Equation (13), is also defined as

$$\kappa_T = \frac{1}{n}\left(\frac{\partial n}{\partial P}\right)_T, \tag{22}$$

where $n = 1/v$.

For a van der Waals gas, κ_T can exhibit non-ideal behavior, especially near phase transitions [11]. For a physically stable system, κ_T should be positive because positive compressibility indicates that the volume decreases as pressure increases, which is the expected response of a stable system to compression. If the isothermal compressibility κ_T

for a van der Waals gas is negative at low densities and suddenly becomes positive at larger densities, this unusual behavior can be interpreted in terms of stability and the nature of phase transitions in the gas.

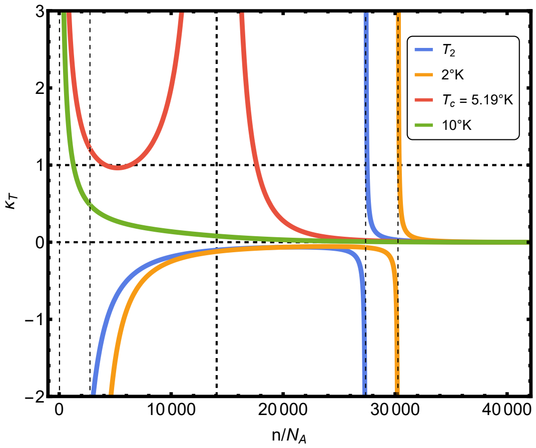

Figure 4. Isothermal compressibility κ_T versus n/N_A for several temperatures: 2 °K, $T_c = 5.19\,°$K, 10 °K, and T_2. The data used correspond to Helium, as given in Table 1. The dashed vertical lines represent the divergences of κ_T.

When κ_T is negative, it implies

$$\left(\frac{\partial v}{\partial P}\right)_T > 0, \quad \text{or} \quad \left(\frac{\partial n}{\partial P}\right)_T < 0, \tag{23}$$

which means that an increase in pressure leads to an increase in volume (or a decrease in density), which is a sign of mechanical instability. Such behavior is non-physical for a stable, homogeneous phase of matter. At low densities, where κ_T is negative, the system may be in a metastable state. This means that small perturbations can cause the system to move toward a more stable state.

In terms of density, the expression for κ_T given by Equation (14) is

$$\kappa_T = \frac{(1-nb)^2}{n(k_B T - 2an(1-nb)^2)}. \tag{24}$$

Note that for a fixed T, divergences occur when $n = 0$ or when $k_B T - 2an(1-nb)^2 = 0$. These are represented as dashed vertical lines in Figure 4.

Divergences in the plot of isothermal compressibility κ_T versus density for a van der Waals gas are evidence of phase transitions [11]. For a vdW gas, κ_T is related to the response of the volume (or density) to changes in pressure at constant temperature. At a critical point (e.g., critical temperatures T_c, T_2), certain thermodynamic quantities exhibit singular behavior. For the vdW gas, near the critical point, the isothermal compressibility can diverge, indicating a phase transition. Within the phase coexistence region, the system can exhibit large fluctuations in volume (or density) for small changes in pressure, leading to large (or diverging) values of κ_T. We thus reconfirm the emergence of a classic–quantum phase transition at T_2.

4. Phase Diagram

We now present, in Figure 5, a type of chart for the state equation in which pressure (temperature) is on the y-axis, density is on the x-axis, and the curves inside represent the temperature (pressure). The three quantities coexist at equilibrium.

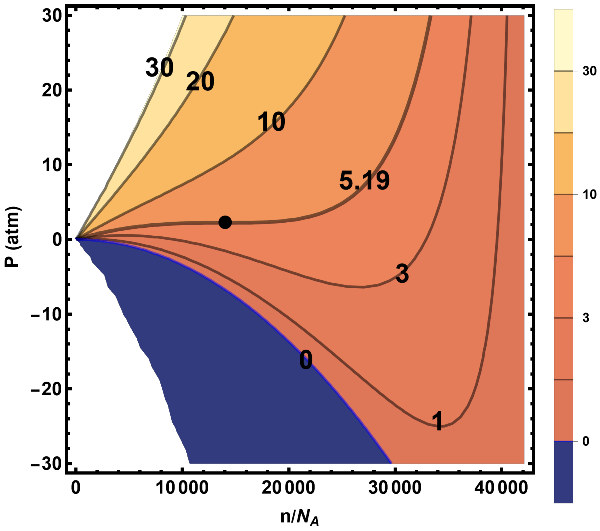

Figure 5. Temperature for given values of the pressure (y-axis) and the density (x-axis). The data used correspond to Helium, as given in Table 1. For Helium, we have T_c = 5.19 °K, P_c = 2.24 atm, and n_c/N_A = 14,064.

The Set of Temperatures T_0

At these temperatures, the pressure P vanishes. It is easy to see that

$$T_0 = \frac{a}{k_B\, n(1-nb)}, \tag{25}$$

so that

$$\begin{array}{lll} P > 0 & \text{for} & T > T_0, \\ P < 0 & \text{for} & T < T_0, \\ P = 0 & \text{for} & T = T_0. \end{array}$$

It is clear that T_0 grows linearly with a. It decreases, also linearly, with b. In Figure 6, we show T_0 as a function of n/N_A.

The expression for T_0 indicates that this special temperature marks a critical point in terms of the behavior of pressure in the van der Waals gas.

The attractive parameter, which represents the extent of particle attraction, is a key factor in determining how pressure behaves. A larger a indicates stronger attractions among molecules.

The density of the gas influences both the number of collisions between molecules and the degree to which the excluded volume affects the system.

$1 - nb$: This term accounts for the effective volume available to the gas molecules after considering their finite size. As the density increases, its value decreases, which can significantly influence the thermodynamic behavior.

Phase Behavior and Pressure Characteristics:

For temperatures $T > T_0$, the pressure is positive, indicating that the gas behaves similarly to an ideal gas, with prevailing repulsive intermolecular forces overcoming the attractive forces. The gas is likely to expand and exhibit typical gas-like behavior.

For temperatures $T < T_0$, the pressure becomes negative, which is non-physical in the sense that it suggests instability in the system. This occurs because the attractive forces dominate, leading to a state where the gas cannot sustain its configuration and is more likely to condense or collapse.

At $T = T_0$, the pressure vanishes, indicating a critical point where the forces balance. This temperature can mark a phase transition or indicate a threshold behavior suggesting an equilibrium between attractive and repulsive forces.

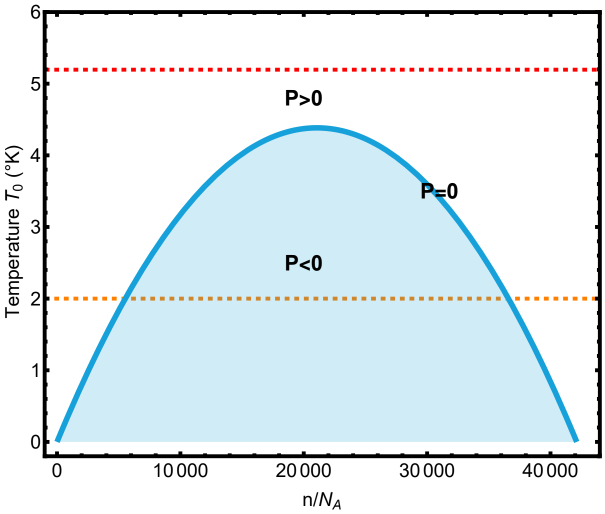

Figure 6. Temperature T_0 versus n/N_A allows one to view the regions where the pressure is positive, negative, or zero. The data used correspond to Helium, as given in Table 1. The red dashed line represents the critical isotherm T_c = 5.19 °K. The pressure is always positive, as we can see in Figure 3. The orange dashed horizontal line corresponds to the isotherm $T = 2$ °K. In this case, we have positive pressures at low and high densities and negative pressures at intermediate densities, as shown in Figure 3.

Physical Interpretation:

The dependence of T_0 on a, n, and b reveals how the nature of intermolecular interactions and the excluded volume influence the thermodynamic properties of the gas. By increasing the density, the effective volume available for motion decreases, influencing the required temperature for stability.

The negative pressure regime suggests a strong correlation with phase transitions that may occur in the gas, such as condensation, toward a liquid or solid state as one approaches T_0 from below or potentially indicating the onset of new phase behaviors.

Applications and Implications: Understanding this temperature and its relationship with pressure can be pivotal in applications involving gases where intermolecular forces are non-negligible, such as in chemical engineering, materials science, and atmospheric science.

It can also serve as a fundamental study point in the classroom to illustrate real gas behavior, critical points, and phase transitions, making the van der Waals equation a key teaching tool in thermodynamics and statistical mechanics.

In summary, the equation for T_0 highlights the critical balance between attractive and repulsive intermolecular forces in a van der Waals gas. The behavior of pressure relative to this special temperature provides important insights into the stability and phase behavior of real gases, emphasizing how molecular interactions, density, and temperature combine to influence thermodynamic properties.

5. Gas Models' Limitations

To explain the limitations of classical gas models, we contrast the assumptions and approaches of classical gas models with the insights provided by Refs. [14,15].

5.1. Classical Gas Models

Classical gas models, such as the ideal gas law or the van der Waals equation, rely on assumptions like those below:

- Particles are point masses with no internal structure.

- Interactions are typically limited to the short range, often modeled by simple pairwise potentials.
- Systems are assumed to be in thermodynamic equilibrium and free from significant external constraints like walls or porous structures.

5.2. Reference to Rarefaction Effects

Rarefaction effects introduce complexities not captured by classical gas models. In nanoscale flows or flows through porous media, the mean free path of gas molecules becomes comparable to the characteristic length scale of the system (e.g., pore size). This leads to non-equilibrium effects, such as the following:

- The breakdown of continuum assumptions, which classical models rely on.
- Knudsen number dependency: Gas behavior becomes dependent on the Knudsen number (the ratio of the molecular mean free path to a characteristic dimension). At high Knudsen numbers, gas particles are more likely to undergo ballistic motion instead of diffusive interactions, making traditional gas laws invalid.
- Boundary and surface interactions dominate, which are not accounted for in classical gas laws, especially in micro- and nanoscale systems. Porous structures modify thermal and flow properties in ways that classical models fail to address.

5.3. Monte Carlo Tree Search (MCTS)

While not directly related to physical gas laws, the MCTS method represents a modern computational tool that helps explore and simulate complex decision-making scenarios or probabilistic systems. Classical gas models often assume simplicity in their solution techniques (analytical or simple numerical methods), which is insufficient for complex or stochastic gas behaviors, especially at the micro-/nanoscale. MCTS has been modified and applied in various fields to optimize search strategies for systems with vast state spaces or uncertain outcomes in the context of gas models.

Probabilistic methods like MCTS highlight the necessity to move beyond deterministic classical gas models, especially when dealing with systems where the phase space is large or stochastic behaviors dominate.

In nanoscale gas flows, where classical models fail to provide accurate predictions due to rarefaction and non-equilibrium effects, the use of stochastic sampling (like in MCTS) can offer better insight and solutions that deterministic classical gas equations cannot handle.

In summary, the paper on rarefaction effects illustrates how classical gas models break down at small scales, where non-equilibrium and surface effects dominate.

The Monte Carlo Tree Search review emphasizes the need for probabilistic and computational approaches to address complex, high-dimensional systems that classical gas models cannot solve effectively.

Both references together showcase how modern methods, either through experimental insights or computational techniques, reveal limitations in the assumptions of classical gas models.

6. Conclusions

In this study, we examined the thermodynamic behavior of van der Waals gases at a specific temperature, T_2, where quantum mechanical effects begin to play a significant role. Our findings offer critical insights into the classical–quantum frontier and the limitations of classical gas behavior descriptions under these conditions. These findings are as follows:

1. Mechanical Instability: At temperatures T_2 for a van der Waals gas, the isothermal compressibility becomes negative, indicating mechanical instability. This suggests that the system can no longer be adequately described by classical thermodynamics alone and requires quantum mechanical considerations.
2. Limitations of Classical Models: In the pressure–volume $(P-V)$ diagram, the pressure becomes negative at very small volumes when the system reaches these critical temperatures. This phenomenon underscores the limitations of classical models,

such as the van der Waals equation, in predicting gas behavior under extreme conditions. Negative pressure signals a mechanically unstable or non-physical region, necessitating phase transitions to more stable configurations.

3. Signatures of the Classical–Quantum Transition: The observed negative isothermal compressibility and pressure are clear indicators of the transition from classical to quantum behavior in gases. These findings emphasize the importance of incorporating quantum effects into thermodynamic analysis, particularly at low temperatures and high densities, where the de Broglie thermal wavelength becomes significant.
4. Macroscopic Manifestations: Our study highlights simple macroscopic manifestations of the classical–quantum transition. The instances of mechanical instability and negative pressures observed here are rare but significant examples of how quantum mechanical effects can dramatically alter macroscopic behavior. These phenomena demonstrate the tangible impact of quantum mechanics on gas behavior, illustrating how quantum properties influence observable macroscopic scales.
5. Fundamental Insights from Simple Systems: It is surprising to find such clear evidence of the classical–quantum frontier in relatively simple systems like van der Waals gases. This suggests that even basic models can yield valuable insights into the transition from classical to quantum behavior, highlighting the fundamental nature of these effects.
6. Implications for Complex Systems: Understanding these transitions in simple gas models provides a foundational framework for studying more complex systems. It enhances our knowledge of gas behavior and phase transitions, offering valuable insights into phenomena such as Bose–Einstein condensation and superfluidity in condensed matter physics.

In summary, our study demonstrates that at specific temperatures, the behavior of gases deviates significantly from classical predictions due to quantum effects. The negative isothermal compressibility and pressure observed at these temperatures mark the onset of quantum mechanical behavior, emphasizing the critical role of quantum effects in determining gas behavior at low temperatures. These findings deepen our understanding of the classical–quantum frontier and pave the way for further research into quantum thermodynamics and its applications.

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