Phase Diagram of Electron–Hole Liquid in Monolayer Heterostructures Based on Transition Metal Dichalcogenides

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Abstract—The interest in monomolecular layers of transition metal dichalcogenides (TMDs), which has been shown in recent years, is due to their peculiar electronic and optical properties that are very attractive for designing functional elements of new-generation nanoelectronics. Experimental proofs of the formation of a high-temperature strongly bound electron–hole liquid (EHL) in TMD monolayers have been obtained recently. Strong coupling of charge carriers is associated with a considerable decrease in screening of the Coulomb interaction in monolayer heterostructures. In this study, the gas–liquid phase transition in the system of electrons and holes in quasi-two-dimensional TMD-based heterostructures is considered and critical parameters of such a transition are calculated. The insulator–metal transition is described and the phase diagram for such heterostructures is constructed.

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1. INTRODUCTION

Recent 15 years have been marked by intense studies of graphene, two dimensional (2D) carbon material, as the basis for new-generation nanoelectronics [1]. This gave rise to active studies of 2D materials such as monolayers of hexagonal boron nitride, black phosphorus, transition metal dichalcogenides (TMDs), as well as many other compounds [2]. The obtaining and studying vertical (van der Waals) heterostructures, in which various 2D materials are combined in a given sequence, has become a promising trend in this activity [3].

Monomolecular TMD layers occupy a special place in current investigations of 2D materials. These compounds have the sandwich structure with a layer of transition metal M encapsulated between layers of chalcogenide X and are described by chemical formula MX\textsubscript{2}. The best-studied representatives of this class of substances are compounds with metal atoms of the VI group (M = Mo, W) and with S, Se, and Te as the chalcogen. Three-dimensional layered TMD such as MoS\textsubscript{2}, WS\textsubscript{2}, MoSe\textsubscript{2}, and WSe\textsubscript{2} have indirect energy gap $E_g$ \approx 1 eV [4, 5], and their monomolecular layers become direct bandgap semiconductors with $E_g$ of about 2 eV [6].

In TMD monolayers, it is possible to obtain the valley-selected excitations of charge carriers by a circularly polarized electromagnetic wave [7–11]. This stimulated the development of devices of new-type nano-electronics (valleytronics), in which along with the electric charge transport, a selective transport of charge carriers with a certain valley index can occur [1, 12–14].

Optical properties of monomolecular TMD layers are determined to a considerable extent by excitons and trions. Exciton binding energy $E_x$ in TMDs amounts to \sim 100 meV, while this energy of trions is \sim 10 meV [6]. The inclusion of TMD layers into the van der Waals heterostructures makes it possible to observe many-particle effects in systems with long lifetimes of charge carriers. For this reason, TMD-based structures are considered ideal systems for studying high-temperature electron–hole liquid (EHL).

The energy of an electron–hole (e–h) pair in EHL [15–20] is usually $|E_{EHL}| \geq E_x$, and the critical temperature of the gas–liquid phase transition is $T_c \sim 0.1|E_{EHL}|$. Therefore, it can be expected that EHL will be observed in TMD monolayers even at room temperature.

In 2019, a number of publications appeared concerning EHL in TMD monolayers. Let us consider...
these works in greater detail to elucidate the state of
the art in this field.

In this connection, we can mention paper [21],
where the results of observation of the electron–hole
plasma (EHP) in MoS₂ monolayer have been
reported. Although the observation of EFL has not
been declared in that publication, important results for
further investigations have been obtained. In particu-
lar, it has been demonstrated that the photoexcitation
of the MoS₂ monolayer leads to a transition from the
direct to indirect bandgap, which facilitates the EHL
formation.

It was shown in [22] that an increase in the inten-
sity of continuous optical excitation of the MoS₂
monolayer in the subgap regime initiates a transition
of the insulating exciton gas to a metallic EHL.

The high-temperature strongly coupled EHL with
$T_c = 500$ K in a suspended MoS₂ monolayer was inves-
tigated in [23]. The first-order gas–liquid phase
transition characterized by the critical density and tem-
perature was observed. For the same excitation, an
EHL differs from EHP in the higher density of charge
carriers and, hence, in stronger photoluminescence.
In experiment, photoluminescence increased jump-
wise when the pumping power increased to approxi-
ately 3 kW/cm². The incompressibility of the EHL
was demonstrated: upon a further increase in the
pump power, the area occupied by EHL increased in
proportion to the number of generated $e$–$h$ pairs,
while EHL density remained unchanged. In experi-
ments, the luminescent ring emerging because of pho-
non wind was observed (see, for example, review [18]
and the references therein).

In [24], EHL in ultrathin graphene–thin (several
monolayers) MoTe₂ film–graphene photocells was
tested at room temperature. When pump laser power $P$
reached a value of 3 mW, the density of $e$–$h$ pairs
became so high that the mean distance between them,
$a_{xx} = 1–3$ nm, was comparable with exciton Bohr
radius $a_e = 2.3$ nm [25]. In these conditions, exciton
annihilation (transition of the insulating exciton gas to
a metallic EHP) was observed. After this, at a higher
value of laser power $P_c = 6$ mW, EHP undergoes the
gas–liquid transition. The formation of 2D EHL drop
was proved by the emergence of a characteristic
dependence of the photocurrent on the pump laser
power and by the photocurrent dynamics on the pico-
second scale. Such a behavior was observed during the
formation of EHL drops in traditional semiconductors
(Si, Ge, GaAs, etc.) at low temperatures [16, 17].

Theoretical work [26] was devoted to calculation of
the EHL phase diagram in a suspended MoS₂ layer.
That study was motivated by experimental results
described in [23]. For calculating the EHL properties
the potential describing the Coulomb interaction of
charge carriers in finite-thickness films (Keldysh
potential [27–29]), was used in [26]. It proved to be
effective for explaining a noticeable deviation of the
energy of several first exciton levels from the Rydberg
series [6].

According to estimates made in [26], the metal–
insulator transition in MoS₂ occurs in the liquid phase
at a density higher than the critical value for the gas–
liquid transition. It should be noted that EHP in an
ultrathin MoTe₂ film is similar in many respects to
EHP in the MoS₂ monolayer; therefore, the metal–
insulator transition in both systems most probably pre-
cedes the gas–liquid transition.

In our opinion, such a qualitative discrepancy is
due to unjustified use of the Keldysh potential in
EHL calculations [26], which shifts the critical point
towards lower densities and temperatures. In the cal-
culation for excitons and EHL, the main contribu-
tions come from substantially different diagrams of
perturbation theory (ladder and loop diagrams, re-
spectively) [30].

The effect of the dielectric environment, as well as
of electron doping (when the electron and hole den-
sities are different) on the EHL phase diagram (gas–liq-
uid and metal–insulator transitions) were investigated
in [31] by the method of spectral functions. The EHL
phase diagram in doped multivalley semiconductors
were considered earlier in [32–34].

It was shown in our previous paper [30] that the
formation of a high-temperature strongly compressed
tightly bound EHL in TMD-based multilayer hetero-
structures is due to suppression of the Coulomb inter-
action screening. The Coulomb interaction of charge
carriers in multilayer films is determined by the half-
sum of the permittivities of the surroundings (for a
sample on a substrate, it is vacuum and the substrate,
while for a suspended sample, it is vacuum). In both
cases, the effective permittivity is substantially smaller
than for TMD films. As a result, EHL with an anom-
ously high ground-state energy $|E_{EHL}|$ amounting to
fractions of an electronvolts and a high density $n_{EHL}$
is formed. For example, the following experimental val-
ues were obtained for a suspended MoS₂ monolayer:
$|E_{EHL}| = 0.48$ eV and $n_{EHL} = 4 \times 10^{15}$ cm⁻² [23].

Proceeding from our previous results, we analyze in
this study the EHL phase diagram in quasi-two-
dimensional heterostructures based on TMD.

The EHL appears due to the first–order phase tran-
sition when charge carrier density (free and/or cou-
ples into excitons) reaches a certain temperature-
dependent critical value $n_G(T)$ of the saturated vapor
density [15]. Critical density $n_G(T_c) = n_c$ of $e$–$h$
pairs is attained at critical temperature $T_c$.

In this study, we analyze the metal–insulator
(Mott) transition occurring at density $n_{dm}(T)$ of $e$–$h$
pairs. With increasing density, this transition usually
precedes the gas–liquid transition ($n_{dm}(T) < n_c$) and
occurs in the gas phase [15, 16].
We will seek for semiconductors films in which the EHL is characterized by the highest binding energy and, hence, the highest critical temperature. To this end, we consider model semiconductors with different numbers of electron and hole valleys and different effective masses of electrons and holes.

2. MODEL CONCEPTS

We describe the model quasi-2D $e\rightarrow h$ system by Hamiltonian [35, 36]

$$H = \sum_{\nu \nu} \left( \sum_{p l} \frac{1 - e^2}{2} p \sigma_{p l} \alpha_{p l} + \sum_{p l} \frac{1 + e^2}{2} p \sigma_{p l} \beta_{p l} \right)$$

$$+ \frac{2}{2} \sum_{p p \nu \nu} V(q) \left( \sum_{k l} a_{n k}^\dagger a_{n k}^\dagger + \sum_{k l} b_{n k}^\dagger b_{n k}^\dagger \right)$$

Note that TMD monolayers have also indirect optical transitions with the generation of an electron in the valley of the $\Lambda$ point (at the middle of segment $\Gamma-K$). This valley is characterized by an energy close to the valley of the $K$ point. In particular, in WSe$_2$, this valley lies lower by approximately 80 meV than the valley of the $K$ point [39]. However, such transitions are substantially more seldom than direct transition at the $K$ point (such transitions require the participation of phonons with a large wavevector of about 1/4 of the Brillouin zone). For this reason, the number of electrons in the valley of the $\Lambda$ point is much smaller than in the valley of the $K$ point (probably, at least by two orders of magnitude). The inclusion of electrons in the valley of the $\Lambda$ point would lead to significant exceedance of the accuracy of EHL calculations; for this reason, we take into account electrons only in the valley of the $K$ point.

In this study, we account for the interaction in EHL using the conventional Coulomb 2D potential $V(q) = 2\pi\bar{e}^2/|q|$ and not the Keldysh potential [26–30]

$$V(q) = \frac{2\pi\bar{e}^2}{|q|(1 + r_0|q|)}$$

where $r_0 = d/2\delta$ is the screening length, $d$ is the thickness of the film, $\delta = \varepsilon_{\text{eff}}/\varepsilon$, $\varepsilon$ is the permittivity of the film material, $\varepsilon_{\text{eff}} = (\varepsilon_1 + \varepsilon_2)/2$ is the effective permittivity of the media surrounding the film (e.g., $\varepsilon_1 = 1$ is the permittivity of vacuum and $\varepsilon_2$ is the permittivity of the substrate), and $\bar{e}^2 = e^2/\varepsilon_{\text{eff}}$. For systems with TMD monolayers, quantity $r_0$ is a fitting parameter used in calculations for excitons [6].

In our previous work [30], we calculated the EHL characteristics using the conventional 2D Coulomb potential and the Keldysh potential in the case of the same degeneration for electrons and holes. It turned out that using only one fitting parameter, it is impossible to match both characteristics being calculated (EHL binding energy and its equilibrium density) with experimental data. It should be noted that screening length $r_0$ is very small (less than 1 Å), and the Keldysh potential actually coincides with the conventional potential.

We refined our results of calculation for the binding energy of an EHL in the suspended MoS$_2$ monolayer with account for different degeneration of electrons, $g_e = 4$ (there are two valleys and degeneracy in spin) and holes, $g_h = 2$ (there are two valleys, but no degeneracy in spin in each valley). For $r_0 \approx 0.30 \text{ Å}$, the EHL binding energy coincides with experimental value (480 meV) [23], although the calculated equilibrium EHL density, $2.4 \times 10^{13} \text{ cm}^{-2}$, turns out to be lower than the experimental value. A further increase in $r_0$ leads to a decrease in $|E_{\text{EHL}}|$ and $n_{\text{EHL}}$. For $r_0 \approx 0.66 \text{ Å}$, the EHL binding energy becomes equal to the exciton
binding energy, and EHL is not formed for higher values of $r_0$.

Calculations show [40] that $r_0 = 41.47 \, \text{Å}$ for an exciton. Such a discrepancy can be explained qualitatively by the fact that apart from the difference in the class of diagrams [30], the expression for $r_0$ also contains different permittivities for the film material (static $\varepsilon_0$ for the exciton and high-frequency permittivity $\varepsilon_\infty$ for EHL) [41]. Since TMDs are polar semiconductors, different permittivities for the film material (static $\varepsilon_0$ for the exciton and high-frequency permittivity $\varepsilon_\infty$ for EHL) [41]. Since TMDs are polar semiconductors, the expression for $r_0$ also contains different permittivities for the film material (static $\varepsilon_0$ for the exciton and high-frequency permittivity $\varepsilon_\infty$ for EHL) [41]. Since TMDs are polar semiconductors, the expression for $r_0$ also contains different permittivities for the film material (static $\varepsilon_0$ for the exciton and high-frequency permittivity $\varepsilon_\infty$ for EHL) [41]. Since TMDs are polar semiconductors, the expression for $r_0$ also contains different permittivities for the film material (static $\varepsilon_0$ for the exciton and high-frequency permittivity $\varepsilon_\infty$ for EHL) [41].

For determining the system of units, we also set $\bar{e}^2 = 1$. Then the binding energy and the 2D exciton radius are automatically equal to unity: $E_x = 2me^2/h^2 = 1$ and $a_x = h^2/2me^2 = 1$. We will assume below that energy and temperature are measured in the units of $E_x$, and the density of $e^{-h}$ pairs is measured in the units of $a_x^{-2}$.

In the next two sections, we will concentrate on the calculation of the ground-state energy of EHL and its thermodynamics in a TMD monolayer using the results obtained earlier for quasi-2D systems [43–45].

3. GROUND-STATE ENERGY

We consider a semiconductor in which the numbers of electron and hole valleys are not necessarily identical. Without loss of generality, we will henceforth assume that $v_e \geq v_h$ (i.e., assume that charge carriers with a larger number of valleys are electrons). We will measure momenta $q$ in the units of $q_T = q_T^e \leq q_T^h$, where $q_T^e$ and $q_T^h$ are the Fermi momenta of electrons and holes, respectively, $q_T^e, q_T^h = \sqrt{2\pi n/v_T}$, $v_T$ will be measured in the units of $q_T^2/2m$. We introduce dimensionless distance $r_q = \sqrt{v_e/v_h}$ between particles, where $n$ is the 2D density of charge carriers.

Here and below, we assume that spin degeneracy is observed for both electrons and holes.

In some cases, the spin–orbit splitting of the valence band in TMD is quite large (e.g., it is 148 meV for MoS$_2$ [26]); then instead of $v_h$, we should use $v_h/2$ (we consider only the upper spin branches of the valence band).

Under intense photoexcitation of a MoTe$_2$ film, holes are accumulated at point $\Gamma$; therefore, $v_h = 1$, while the number of electron valleys remains unchanged, and $v_e = 2$ [24].

The ground-state energy of a 2D EHL per $e^{-h}$ pair is given by [30, 35, 36]

$$E_{gs} = E_{kin} + E_{exch} + E_{corr}.$$  \hspace{1cm} (3)

The first term is kinetic energy ($\chi = v_e/v_h$ and $\chi \geq 1$)

$$E_{kin} = \frac{1 + \chi \sigma}{1 + \sigma} r_q^{-2}. \hspace{1cm} (4)$$

The second term is exchange energy

$$E_{exch} = -\frac{4\sqrt{\chi}}{3\pi} (1 + \sqrt{\chi}) r_q^{-1}. \hspace{1cm} (5)$$

The third term is the correlation energy that is presented in the form of the integral over the transferred momentum [30, 35, 36, 46, 47],

$$E_{corr} = \int_0^\infty I(q) dq. \hspace{1cm} (6)$$

For $q \ll 1$, we are using the random phase approximation (RPA) [35, 36, 46, 47]. Function $I(q)$ for $q \gg 1$ is determined by the sum of second-order interaction diagrams (Fig. 1). In the intermediate range, function $I(q)$ is approximated by a segment of a tangent [30, 35, 36].

For arbitrary values of $\sigma$ and $\chi$, the expansion of function $I(q)$ for small $q$ is quite cumbersome. For identical masses of the electron and the hole ($\sigma = 1$) and identical numbers of electron and hole valleys ($\chi = 1$), this expansion was given in our previous paper [30].

The terms in $I(q)$ for $q \ll 1$ with half-integer powers of $q$ are the contribution from a 2D plasmon:

$$\omega(q) = 2^{1/4} (v_e r_q q)^{1/2} + \frac{3}{2^{3/4} (v_e r_q)^{1/2}} \left( \frac{1}{\eta_e} + \frac{\chi}{\eta_h} \right) q^{3/2}. \hspace{1cm} (7)$$

Here, $\eta_e = m_e/m = 1 + \sigma$ and $\eta_h = m_h/m = 1 + \sigma^{-1}$.

It is interesting to note that in contrast to the 3D case, in the 2D case, there also exists a branch of decaying excitations,

$$\omega_0(q) = \frac{2}{\eta_e} q - \frac{1}{\eta_e} q^2 + \frac{1}{\eta_e} \left( 1 + \frac{1}{\chi \sigma} \right)^2 q^3. \hspace{1cm} (8)$$
If inequalities
\[
1 + \kappa \sigma < \sigma \sqrt{\kappa(1 + 2\kappa \sigma)}, \\
1 + \kappa \sigma > \frac{\sigma^2 \kappa^{3/2}}{\sqrt{\sigma^2 \kappa - 1}}
\]
hold, two more branches of damped oscillations are possible:

\[
\omega_1(q) = \frac{2(1 + \kappa \sigma)}{\eta_a \sqrt{1 + 2\kappa \sigma}} q - \frac{2\sqrt{2} \kappa^3 \sigma^2 q^2}{\nu_v \eta_b^2 r_n^2 (1 + 2\kappa \sigma)^{3/2}} \\
- \frac{2(1 + \kappa \sigma)}{\eta_a \sqrt{1 + 2\kappa \sigma}} \left[ \frac{3\kappa^6 \sigma^6}{\nu_v^3 \eta_b^2 r_n^2 (1 + 2\kappa \sigma)^3} + \frac{1}{8} \right] q^3
\]

\[
\omega_2(q) = \frac{2\sqrt{2} \kappa^2 q}{\eta_b} - \frac{1}{\eta_b} q^2 \\
+ \frac{1}{\eta_b \sqrt{\kappa}} \left( 1 + \kappa \sigma - \frac{\sigma^2 \kappa^{3/2}}{\sqrt{\sigma^2 \kappa - 1}} \right)^2 q^3.
\]

We presume that the most frequent case when \( \sigma \sqrt{\kappa} > 1 \) is realized (for many TMDs, \( \sigma = 0.73-1.12 \), and ratio \( \kappa \geq 2 \) for \( \nu_v \neq \nu_h \)).

Inequalities (9) hold for \( \sigma > \sigma_c(\kappa) \),

\[
\sigma_c(\kappa) = \frac{1.032 \kappa^{3/4}}{\kappa - 0.136}.
\]

In particular, \( \sigma_c(2) = 0.931 \). Function \( \sigma_c(\kappa) \) is plotted in Fig. 2.

The presence of additional branches (8), (10), and (11), which are absent in the 3D case, apparently ensures strong coupling of a 2D EHL.

Equilibrium EHL energy \( E_{\text{EHL}} \) is the minimum of ground-state energy \( E_{\text{gs}} \),

\[
\left. \frac{\partial E_{\text{gs}}}{\partial n} \right|_{n_{\text{EHL}}} = 0, \quad E_{\text{EHL}} = E_{\text{gs}}(n_{\text{EHL}}),
\]

where \( n_{\text{EHL}} \) is the equilibrium EHL density.

The equation for \( n_{\text{EHL}} \),

\[
1 + \kappa \sigma \frac{\pi}{\nu_c} - \frac{2\sqrt{2}(1 + \sqrt{\kappa})}{3\sqrt{3} \nu_c n_{\text{EHL}}} + \left. \frac{\partial E_{\text{corr}}}{\partial n} \right|_{n_{\text{EHL}}} = 0
\]

is very cumbersome and is not given here for brevity. In the case of equal numbers of electron and hole valleys, we can use Eqs. (21) and (22) from our previous work [30] for determining \( n_{\text{EHL}} \) and \( E_{\text{EHL}} \), respectively.

4. THERMODYNAMICS OF THE MONOLAYER

Proceeding from analogy of nonequilibrium charge carriers in semiconductors with electrons and ions in crystals, Keldysh [48] proposed that upon a decrease in temperature or upon an increase in the density of the exciton or exciton molecule (biexcitons) gas, liquefaction of this gas will occur in EHL, and the system would undergo the first-order gas—liquid phase tran-

sition. Since the end of 1960s, the EHL formation has been observed in many semiconductors (see, for example, [16–20] and the references therein).

On the \((n, T)\) plane, the gas—liquid transition corresponds to a bell-shaped curve with critical point \((n_c, T_c)\) at the top. This curve passes through points \( n = n_0 \) and \( n = n_{\text{EHL}} \) at \( T = 0 \). The value of \( n_0 \) is determined by equality \( |E_{\text{EHL}}| = E_x + E_D/2 \), where \( E_D \) is the biexcitons dissociation energy [17]. The domain on the left of the \( n_0 \) branch emerging from point \((n_0, 0)\) corresponds to the (bi)exciton insulating gas; on the right of the \( n_L \) branch emerging from point \((n_{\text{EHL}}, 0)\), the EHL domain is located. An unstable domain lies under the bell, where the separation into EHL droplets with density \( n_L \) and the saturated vapor of excitons or \( e^-h \) pairs with density \( n_c \) occurs.

The phase diagram also contains the second bell-shaped curve that corresponds to the exciton—plasma (insulator—metal) transition. It is difficult to construct this curve for arbitrary densities and temperatures, and we confine our analysis to estimates only in the most interesting domains. In the classical domain \((T \gg E_F)\), an increase in the density of excitons leads to their dissociation; for this reason, the transition of excitons to exciton–plasma transition are those in which band degeneracy reduces the EHL stability, and \( T_c \) decreases. For this reason, exciton gas densities close

![Fig. 2. Numerically calculated \( \sigma_c(\kappa) \).](image-url)
Table 1. Critical point of the gas–liquid transition and parameters of a 2D EHL in TMD monolayers

| \((v_e, v_h)\)  | (1, 1) | (2, 1) | (2, 2) | (4, 1) | (4, 4) |
|----------------|--------|--------|--------|--------|--------|
| \(n_c\)       | 0.035  | 0.054  | 0.089  | 0.075  | 0.242  |
| \(T_c\)       | 0.136  | 0.164  | 0.196  | 0.198  | 0.294  |
| \(n_{EHL}\)   | 0.164  | 0.264  | 0.450  | 0.394  | 1.302  |
| \(|E_{EHL}|\)  | 1.090  | 1.340  | 1.661  | 1.606  | 2.545  |
| \(n_{EHL}/n_c\) | 4.686  | 4.889  | 5.056  | 5.253  | 5.379  |
| \(|E_{EHL}|/T_c\) | 8.015  | 8.171  | 8.111  | 8.070  | 8.718  |

The right-hand side of this expression is chemical potential \(\mu_{\text{kin}}\) of noninteracting particles (first term) together with exchange (\(\mu_{\text{exch}}\)) and correlation (\(\mu_{\text{corr}}\)) contributions (second and third term, respectively). In expression (13), we have disregarded the temperature dependences of \(\mu_{\text{exch}}\) and \(\mu_{\text{corr}}\) because temperature corrections to \(\mu_{\text{exch}}\) and \(\mu_{\text{corr}}\) are mutually canceled for \(T \ll E_c\). This is in conformity with the results obtained earlier for the 3D case [17, 62, 63].

Critical point \((n_c, T_c)\) of the gas–liquid transition is determined by the following two equations:

\[
\frac{\partial \mu}{\partial n} \text{at } T = T_c = 0, \quad \frac{\partial^2 \mu}{\partial n^2} \text{at } T = T_c = 0. \tag{14}
\]

To verify our methods for investigating the phase diagram of EHL in TMD monolayers, we calculated the similarity relationship \(T_c \approx 0.1|E_{EHL}|\) typical of the gas–liquid transition in general (see the footnote in p. 272 of monograph [64]) [15], as well as ratio \(n_e/n_{EHL} \approx 0.2\) of the critical density to the equilibrium density, which is typical of a low-temperature EHL [17].

Table 1 contains the results of numerical solution of Eqs. (14) for \(\sigma = 1\). It should be noted that for a relatively small number of valleys, ratio \(|E_{EHL}|/T_c\) is almost independent of the number of valleys. This ratio attains its maximal value for \(v_e = v_h = 4\), which is possible for Mo0W1 – xS2 alloy with valleys of MoS2 and WS2 with equivalent energies.

The results of numerical calculation of ratios \(n_{EHL}/n_c\) and \(|E_{EHL}|/T_c\) for different numbers of valleys are shown in Fig. 3.

For \(\sigma = 1\), domain \(v_e = v_h \gg 1\) (right upper part in upper panels of Fig. 3) corresponds to ratios \(n_{EHL}/n_c\) and \(|E_{EHL}|/T_c\), which are close to maximal values.

For \(v_e = 1, v_h \gg 5\) or for \(v_h = 1, v_e \gg 5\), ratio \(n_{EHL}/n_c\) is close to maximum, while \(|E_{EHL}|/T_c\) tends to minimum. This is explained by a more rapid increase in \(T_c\) as compared to \(|E_{EHL}|\) in these domains.

For \(\sigma \neq 1\) (here, we set \(\sigma = 0.8\), see lower left panel in Fig. 3), ratio \(n_{EHL}/n_c\) noticeably changes: the minimum is shifted to the domain with large values of \(v_e\) and small values of \(v_h\); the maximal remain in the domain of large \(v_h\) and small \(v_e\) for \(v_e = v_h \geqslant 1\), intermediate values are observed. It is interesting to note that no such rearrangement is observed for a more fundamental ratio \(|E_{EHL}|/T_c\), and changes occur

to \(n_c\) can be realized in such semiconductors at low temperatures. For example, it was found experimentally that the metal–insulator transition in uniaxially deformed Ge occurs at \(r_e = 2 \pm 0.1\). This agrees well with estimate \(r_e \approx 1.8\), which was obtained using dielectric screening of excitons [49].

The three-component system (EHL, free excitons, and free charge carriers) was considered in [53, 54].

Thermodynamic properties of EHL in quasi-2D systems were calculated earlier in [43–45]. Such materials as TMD monolayers and graphene are 2D crystals. The thermodynamics of \(e–h\) systems is equally applicable to quasi-2D heterostructures and to 2D crystals. However, the stability of the latter systems to atomic vibrations across the plane of the crystal is doubtful [55]. In addition, local overheating of the sample can occur during intense photoexcitation. This can lead to local deformation of the crystal lattice and to melting of a 2D crystal [56–60]. The experimentally observed intense photoluminescence leads to the conclusion about complete absence of defects in TMD monolayers. The nonradiative recombination of charge carriers at defects would lead to luminescence quenching. We believe that the melting temperature substantially exceeds the critical temperature \(T_c\) of the gas–liquid transition, and intense photoexcitation of a 2D crystal can lead only to the removal of valley degeneracy that has been observed, for example, in ultrathin MoTe2 film [24].

In the systems considered here, \(e–h\) pairs in different spin and valley states are characterized by different lifetimes. Relaxation times typical of such systems are close to 10 fs [61], which is much shorter than their lifetimes. For this reason, we assume that thermodynamic equilibrium has time for stabilization for all charge carriers.

The chemical potential of an ensemble of \(e–h\) pairs in a TMD monolayer can be written in form [44, 45]
mainly in domain with $\nu_e = 1$, $\nu_h \approx 5$ (see the lower right panel in Fig. 3).

In the limit of a large number of valleys ($\nu_e = \nu_h = \nu \to \infty$), the correlation energy in expression (13) is a power function of density:

$$ E_{\text{corr}} = -A(\sigma) n^\gamma. $$

For 2D systems, exponent $\gamma = 1/3$. Function $A(\sigma)$ was determined in our previous publication [30]. In particular, $A(1) \approx 4.774$.

In the limit $\nu \to \infty$, we can disregard the exchange contribution to energy as well as to chemical potential. In this case, the pair of equations (14) is reduced [15] to equation...
In the particular case when $\sigma = 1$, Eq. (16) is simplified significantly:

$$z_c = (1 - \gamma)(e^{z_c} - 1).$$  \hspace{1cm} (22)

For $\gamma = 1/3$, it has solution $z_c = 0.7627$; in this case, $n_{\text{EHL}}/n_c = 4.7133$ and $|E_{\text{EHL}}|/T_c = 7.1896,$

$$n_c = \left[ \frac{\gamma(1 + \gamma)Av}{2\pi(1 - \gamma)} \right]^{1/(1 - \gamma)} \approx 0.077v^{3/2},$$  \hspace{1cm} (23)

$$T_c = \frac{\sqrt{\pi}}{\sqrt{z_c}} \left[ \frac{\gamma(1 + \gamma)Av}{2\pi(1 - \gamma)} e^{-z_c} \right]^{1/(1 - \gamma)} \approx 0.315v^{1/2},$$  \hspace{1cm} (24)

$$\mu_c = -2 \frac{1 - \gamma + z_c - \ln z_c}{\gamma} T_c \approx -8.307T_c.$$  \hspace{1cm} (25)

To a high degree of accuracy, function $z_c(\sigma)$ is obtained by expanding the right-hand side of Eq. (16) into a series in $z_c$ up to third-order terms:

$$z_c(\sigma) = \frac{3}{2(1 + \zeta^2)} \left[ 1 + \frac{8\sigma}{3(1 - \gamma)}(1 + \zeta^2) - 1 \right],$$  \hspace{1cm} (26)

then

$$n_c = \left[ \frac{\gamma(1 + \gamma)Av}{2\pi(1 - \gamma)} \right]^{1/(1 - \gamma)} \approx 0.077v^{3/2},$$  \hspace{1cm} (27)

$$T_c = \frac{\sqrt{\pi}}{\sqrt{z_c}} \left[ \frac{\gamma(1 + \gamma)Av}{2\pi(1 - \gamma)} e^{-z_c} \right]^{1/(1 - \gamma)} \approx 0.315v^{1/2},$$  \hspace{1cm} (28)

$$\mu_c = -T_c \left[ \frac{2}{\gamma(1 - \gamma)} \left( 1 + \frac{1 - \zeta^2}{12} \right) \right].$$  \hspace{1cm} (29)

For obtaining the temperature dependence of densities $n_{\text{G}}(T)$ and $n_{\text{L}}(T)$ of $e$-$h$ pairs in the gas and liquid phases, we can use the Maxwell construction

$$\int_{n_{\text{G}}}^{n_{\text{L}}} \mu(n, T)dn = \mu(T)(n_{\text{L}} - n_{\text{G}}),$$  \hspace{1cm} (30)

where $\mu(T) = \mu(n_{\text{G}}, T) = \mu(n_{\text{L}}, T)$.

The set of pairs of points $n_{\text{G}}$ and $n_{\text{L}}$ forms a bell-shaped curve on the $(n, T)$ plane. Two typical curves for the TMD monolayer with $v_e = 2$ and $v_h = 1$ and $v_e = v_h = 2$ for $\sigma = 1$ are shown in Fig. 5.

For $v \gg 1$, we obtain the temperature dependences of the density of $e$-$h$ pairs in the gas and liquid phases and of the chemical potential near critical point $T_c - T \ll T_c$ with the same accuracy as in expression (26):

$$n_c - n_{\text{G}}(T) = n_c(T) - n_c \approx \left[ \frac{\sqrt{6}}{\gamma} \left( 1 + \frac{1 - \zeta^2}{12} \right) \right]^{1/2} n_c \left( \frac{T_c - T}{T_c} \right)^{1/2},$$  \hspace{1cm} (31)

$$\mu(T) - \mu_c = 2 - \ln(1 - \zeta^2) + \frac{1 + \zeta^2}{12}(T_c - T).$$  \hspace{1cm} (32)
At low temperatures $T \ll T_c$, the density in the gas phase is exponentially low:

$$n_G(T) = \frac{\nu T}{\pi \sqrt{1 - \frac{\pi^2}{6(1 - \xi^2)}}} e^{-\mu_0/2T}, \quad (33)$$

where $\mu_0 = \mu(n_{EHL}, T = 0) = E_{EHL}$. In the liquid phase, it deviates quadratically in temperature from the equilibrium EHL density $n_{EHL}$:

$$n_L(T) = n_{EHL} \left\{ 1 - \frac{\pi^2}{6(1 - \xi^2)} \left( \frac{1 - \gamma}{2} \right)^{(1 + \nu)/(1 - \nu)} \times \left( 1 + \gamma \right)^{2/(1 - \nu) \frac{\sigma_2}{2} (1 + \gamma)} \left( \frac{T}{T_c} \right)^2 \right\} \quad \text{and} \quad (34)$$

The correction to the chemical potential is also quadratic in temperature:

$$\mu(T) = \mu_0 \left\{ 1 + \frac{\pi^2 \gamma}{6(1 - \xi^2)} \left( \frac{1 - \gamma}{2} \right)^{(1 + \nu)/(1 - \nu)} \times \left( 1 + \gamma \right)^{2/(1 - \nu) \frac{\sigma_2}{2} (1 + \gamma)} \left( \frac{T}{T_c} \right)^2 \right\} \quad \text{and} \quad (35)$$

Equations (16)–(22) and (26)–(35) were written for an arbitrary $\gamma$ since these equations will be required for analyzing 3D layered systems when $\gamma = 1/4$. The corresponding expressions were given in [15].

Generally speaking, the TMD monolayer is a three-layer system, in which a layer of transition atoms is encapsulated between two layers of chalcogen atoms. For this reason, the relevant value of the exponent in the expression for correlation energy can be intermediate between 1/4 and 1/3.

In the case of a finite number of valleys, it is possible to select the effective exponent $\gamma$ in expression (15) for the correlation energy so that simple approximate calculations agree with exact ones. For this purpose, the following two criteria can be proposed: (i) from the coincidence of $n_{EHL}/n_c$ with that obtained from Eq. (20) and (ii) from the coincidence of $|E_{EHL}|/n_c$ with that obtained from Eq. (21).

Proceeding from the data compiled in Table 1, we calculated effective values of $\gamma$ for $\sigma = 1$ using both criteria: $\gamma_e$ from the first criterion and $\gamma_T$ from the second criterion (see Table 2).

The case of finite values of $v$ can differ significantly from the limiting case when $v \rightarrow \infty$. In the single-valley semiconductor, when expression (15) for the correlation energy is hardly operative, $\gamma_e > 1/3$. The coincidence of $\gamma_e$ and $\gamma_T$ is improved with increasing number of valleys. For $v_e = v_h = 4$, the number of valleys is quite large, and $\gamma_e \approx \gamma_T \approx 0.28$, and the choice of the criterion is immaterial. In this case, the effective exponent is closer to the value of $\gamma = 1/4$ for a layered system than to 1/3, which indicates analogy between multivalley and multilayer systems.

![Fig. 5](image-url)

**Fig. 5.** Numerical calculation of $n_G(T)$ and $n_L(T)$ for $v_e = 2$ and $v_h = 1$ (red curve) and $v_e = v_h = 2$ (violet curve) for $\sigma = 1$. Circles indicate the critical points of the gas–liquid transition. Dashed segments of the curves in the range of low charge carrier densities indicate the regions where RPA becomes inapplicable.

For a small number (one or two electron (hole) valleys), it is necessary to choose the appropriate criterion. Numerical calculations of phase diagrams for systems with $v_e = 2$, $v_h = 1$ and $v_e = v_h = 2$ have demonstrated (based on Eq. (15)) better agreement with the curves calculated earlier (see Fig. 5) for effective exponent $\gamma_T$. Therefore, the second criterion is more exact in our opinion.

The results obtained for effective exponent $\gamma$ can be used for calculating the exchange–correlation contribution in the density functional method [65–68].

### 5. Metal–Insulator Transition in the Monolayer

The qualitative difference between theoretical work [26] and experiment [24] was mentioned in Introduction. In experiment with increasing excitation, the metal–insulator transition preceded the gas–liquid transition; i.e., the metal–insulator transition occurred in the gas phase, while theoretical calculations predicted that this transition should occur in the liquid phase. It was noted that this discrepancy appeared because of unjustified use of the Keldysh potential for calculating the ground-state energy.

| $\nu_e, \nu_h$ | (1, 1) | (2, 1) | (2, 2) | (4, 1) | (4, 4) |
|---------------|--------|--------|--------|--------|--------|
| $\gamma_e$    | 0.341  | 0.320  | 0.305  | 0.291  | 0.281  |
| $\gamma_T$    | 0.300  | 0.296  | 0.285  | 0.299  | 0.280  |
| $A_e$         | 2.976  | 3.006  | 3.021  | 3.121  | 3.313  |
| $A_T$         | 2.763  | 2.910  | 2.974  | 3.143  | 3.314  |
Table 3. Parameters of TMD monolayers and calculated ($E_{\text{exc}}(0)$) and experimental ($E_p$) values of the exciton binding energy; $m_0$ is the free electron mass.

| Heterostructure  | $m$, $m_0$   | $r_0$, Å | $\varepsilon_{\text{eff}}$ | $|E_{\text{exc}}(0)|$, meV | $E_p$, meV | References |
|------------------|--------------|---------|-----------------|-----------------|-----------|------------|
| MoS$_2$/SiO$_2$  | 0.320 ± 0.04 | 16.926  | 2.45            | 336             | 310 ± 40  | [38, 40, 71] |
| hBN/MoS$_2$/hBN | 0.275 ± 0.015| 7.640   | 4.45            | 215             | 221 ± 3   | [73]       |
| hBN/MoSe$_2$/hBN| 0.350 ± 0.015| 8.864   | 4.4             | 226             | 231 ± 3   | [73]       |
| hBN/MoTe$_2$/hBN| 0.360 ± 0.04 | 14.546  | 4.4             | 173             | 177 ± 3   | [73]       |
| WS$_2$/SiO$_2$   | 0.220        | 15.464  | 2.45            | 310             | 360 ± 60  | [40, 71, 74]| |
| hBN/WS$_2$/hBN  | 0.175 ± 0.007| 7.816   | 4.35            | 175             | 180 ± 3   | [73]       |
| WSe$_2$/SiO$_2$  | 0.230        | 18.414  | 2.45            | 283             | 370       | [40, 74, 75]| |
| hBN/WSe$_2$/hBN | 0.200 ± 0.01 | 10      | 4.5             | 158             | 167 ± 3   | [73]       |

In [26], equality $|\delta E_g| = E_x$, where $\delta E_g$ is the renormalization of the bandgap, $E_g = E_g^{(0)} + \delta E_g$ ($E_g^{(0)}$ is the initial value of the bandgap), $\delta E_g = \mu_{\text{exch}} + \mu_{\text{corr}}$, was used as the criterion for the emergence of the metal–insulator transition. This corresponds qualitatively to the “crawling” of the bottom of the conduction band upon an increase in the density of $e$–$h$ pairs onto the exciton level if its position is assumed unchanged. In our opinion, such a criterion is incorrect because it disregards the screening of the Coulomb interaction for a high density of $e$–$h$ pairs. We “arrive” at the metal–insulator transition from the side of low densities. In this range of densities, the renormalization of the bandgap can be ignored because the density of free $e$–$h$ pairs in the insulating (exciton) phase is low.

As the criterion of the metal–insulator transition, we are using the vanishing of the ground-state (binding) energy of the exciton,

$$ E_{\text{exc}}(n_{\text{dm}}) = 0. \quad (36) $$

Here, $n_{\text{dm}}$ is the density of this transition.

To find the $E_{\text{exc}}(n)$ dependence, we solve the Schrödinger equation by the variational method in the momentum representation,

$$ \frac{p^2}{2m} \psi(p) - \int \frac{d^2q}{(2\pi)^2} V(q) \psi(q-p) = E_{\text{exc}} \psi(p) \quad (37) $$

($m$ is the reduced mass of the electron and the hole).

The screened Coulomb potential for a high density of $e$–$h$ pairs is given by [44, 45, 69]

$$ V(q) = \frac{V_0(q)}{1 + f(q)\rho_0(q)\Pi_0(q)}, \quad (38) $$

where the initial unscreened Coulomb interaction potential $V_0(q)$ is taken in the form of Keldysh potential (2), $\Pi_0(q)$ is the static 2D polarization operator of electrons and holes,

$$ \Pi_0(q) = \nu_e \Pi_{0,e}(q) + \nu_h \Pi_{0,h}(q), \quad (39) $$

$$ \Pi_{0,e}(q) = m_e \frac{\pi}{\mu_{\text{exch}}} \left(1 - \sqrt{1 - \left(\frac{2q_{\text{ex}}}{q}\right)^2} \theta(q - 2q_{\text{ex}})\right). $$

Here, $\theta(x)$ is the Heaviside function,

$$ \theta(x) = \begin{cases} 0, & x < 0, \\ 1, & x > 0. \end{cases} $$

The polarization operator is taken in the static limit because we are interested in vanishing of the exciton binding energy. Quantity $\Pi_0(q)$ differs from that used in [44, 69] in that the expression for $\Pi_0(q)$ takes into account the existence of several valleys ($\nu_e$ electron and $\nu_h$ hole valleys).

Function $f(q)$ is the Hubbard correction to RPA, which takes into account the contribution of exchange diagrams for large transferred momenta [44, 69, 70]. For equal numbers of valleys $\nu_e = \nu_h = \nu \geq 1$, we have

$$ f(q) = 1 - \frac{1}{4\nu q + q_{\text{F}}} \quad (40) $$

Here, it is considered that the number of exchange diagrams increases linearly in $\nu$, while the number of loop diagrams increases quadratically in $\nu$. For this reason, the relative contribution of the former diagrams decreases as $1/\nu$.

For $\nu_e \neq \nu_h$, the Fermi momenta of electrons and holes are different, and it is convenient to take their geometrical mean $q_{\text{F}} = \sqrt{q_{\text{F,e}} q_{\text{F,h}}}$, which gives

$$ f(q) = 1 - \frac{1}{2(\nu_e + \nu_h) q + q_{\text{F}}} \quad (41) $$

The trial wavefunction is chosen in the form of the Fourier transform of the exponentially decreasing wavefunction of a 2D exciton ($a$ is the variational parameter):

$$ \psi(p) = \frac{\sqrt{8\pi a^2}}{(a^2 + p^2)^{3/2}}. \quad (42) $$
First, we verified the correctness of variational calculations for zero charge carrier density \( n = 0 \). Table 3 compiles the theoretical and experimental data on the exciton binding energy for eight heterostructures.

For calculating the exciton binding energy in the MoS\(_2\) monolayer on the SiO\(_2\) substrate (MoS\(_2\)/SiO\(_2\)), the effective masses of electron and hole were taken from experiment [38]. The values of screening length \( r_0 \) was taken from theoretical work [40]. Our result was compared with the experimental exciton binding energy [71]. A close value of binding energy (340 meV) was obtained by variational solution of the Schrödinger equation in the coordinate space [72].

Experimental data for TMD monolayers encapsulated in thin layers of hexagonal boron nitride (hBN) were taken from [73].

For WS\(_2\) and WSe\(_2\) on the SiO\(_2\) substrate (WS\(_2\)/SiO\(_2\) and WSe\(_2\)/SiO\(_2\)), the parameters for calculations were determined in [40, 74]. Experimental binding energies of excitons in WS\(_2\)/SiO\(_2\) and WSe\(_2\)/SiO\(_2\) were obtained in [71] and [75], respectively.

For MoS\(_2\)/SiO\(_2\) and WSe\(_2\)/SiO\(_2\) heterostructures, the binding energy calculated here fall into the interval of experimental errors. For other heterostructures, good agreement between the calculated and experimental values was also obtained except for WSe\(_2\)/SiO\(_2\), for which the error interval was not given in [75]. As follows from Table 3, good agreement was attained in the whole between the results of our calculations and experimental data.

We also calculated the dependence of binding energy \( |E_{\text{exc}}(0)| \) on \( r_0 \) (Fig. 6). It should be noted that the error intervals for experimental values of binding energy in dimensionless form now appeared on the abscissa axis also because the unit of \( a_c \), measurement, which was used for obtaining dimensionless values of \( r_0 \), contains the error due to inaccuracy in the measurement of effective masses of charge carriers. For the same reason, inaccuracies in \( E_x \) also introduce an additional error into quantity \( E_{\text{exc}}(0) \) in dimensionless form. The experimental points for all heterostructures (except WSe\(_2\)/SiO\(_2\)) with account for errors coincide with the theoretical curve. In [75], binding energy \( E_0 \)
of excitons for the WSe$_2$/SiO$_2$ was apparently calculated for a sample suspended in vacuum, which resulted in a too high value of $E_0$.

We arrive at the conclusion that the above-described method of the variational solution of the Schrödinger equation is applicable to determining the exciton binding energy for zero density of $e$–$h$ pairs.

We have analyzed the dependence of density $n_{dm}$ of the metal–insulator transition at zero temperature on screening length $r_0$ for different numbers of electron and hole valleys and different ratios of charge carrier masses ($\sigma = 0.8–1.1$). The resulting $n_{dm}(r_0)$ curves for different $v_e, h$ and $\sigma$ turned out to be very close. We compared the results of our calculations for $v_e = v_h = 2$ with those reported in [69] for $v_e = v_h = 1$ (Fig. 7). In region $1 \leq r_0 \leq 10$, the values of $n_{dm}$ were also quite close to the theoretical curve. This leads to the conclusion that the dependence of $n_{dm}$ on $v_e, v_h$, and $\sigma$.

For calculating the dependence of the exciton binding energy on the density of $e$–$h$ pairs at $T \neq 0$, we need the polarization operator at a finite temperature. After summation over discrete Matsubara frequencies and analytic continuation to real frequency, we obtain its real part at the real frequency at zero frequency in form

$$\Pi_0(q, T) = v_e \Pi_0^e(q, T) + v_h \Pi_0^h(q, T),$$

$$\Pi_0^\alpha(q, T) = 2 \int \frac{d^2k}{(2\pi)^2} \frac{n^\alpha_T(k) - n^\alpha_T(k + q)}{\varepsilon^\alpha_{k+q} - \varepsilon^\alpha_k},$$

where

$$n^\alpha_T(p) = 1/[\exp(\varepsilon^\alpha_T - \mu^\alpha_{kin})/T] + 1]$$

is the Fermi distribution function of particles of the $\alpha$ species ($\alpha = e, h$) with chemical potential $\mu^\alpha_{kin}$ (calculated for a gas of noninteracting particles), and

$$\varepsilon^\alpha_T = \frac{p^2}{2m_e} + \frac{1}{2} \frac{\varepsilon^\alpha_{kin}}{\eta_\alpha}$$

is the dispersion relation for particles of the $\alpha$ species (the plus sign corresponds to electrons and the minus sign, for holes). The bar on the integral symbol indicates that it is taken in the sense of the principal value.

Using the values of $m, r_0$, and $\varepsilon_{kin}$ from Table 3, we calculated the temperature dependences of density $n_{dm}(T)$ of the metal–insulator transition for heterostructures MoS$_2$/SiO$_2$ and hBN/MoS$_2$/hBN and compared them with the curve in Fig. 8 describing the gas–liquid transition. The points of intersection of the curves on the $(n, T)$ phase diagrams are as follows: $n_{dm} = 0.029 \times 10^{12}$ cm$^{-2}$ at $T_{dm} = 0.164$ (638 K) for the first heterostructure and $n_{dm} = 0.060 \times 10^{12}$ cm$^{-2}$ at $T_{dm} = 0.165$ (412 K) for the second heterostructure. The critical point for the gas–liquid transition is $n_c = 0.055$ (5.5 $\times$ 10$^{12}$ cm$^{-2}$ and 4.2 $\times$ 10$^{12}$ cm$^{-2}$ for the first and second heterostructure, respectively) lies between these points. Consequently, the transition in MoS$_2$/SiO$_2$ occurs in the gas phase, while in hBN/MoS$_2$/hBN, it occurs in the liquid phase.

It should be noted that quantities $n_c$ and $n_{dm}$ for heterostructure hBN/MoS$_2$/hBN are very close (the difference is $\approx 10\%$), and it can be stated with confidence that the transition occurs in the liquid phase. The refinement of calculations of $n_{dm}$ using dielectric screening [50] deserves special analysis.

6. CONCLUSIONS

In this study, we have calculated the phase diagram of an EHL in monolayer heterostructures based on TMD for arbitrary ratios of electron and hole masses and the numbers of valleys.

We have demonstrated that in the multivalley case, the main contribution to the EHL formation comes from the correlation energy. Calculations have shown that the binding energy and the equilibrium EHL density are the higher the larger the number of valleys in TMD. It should be noted that for identical total numbers of valleys, the maximal values are attained for the identical numbers of electron and hole valleys.

We have shown that relation $T_c = 0.1|E_{EHL}|$ between the critical temperature of the gas–liquid transition and the EHL binding energy holds with a good accuracy for various heterostructures.

The method developed in this study has made it possible to determine the power-law dependence $E_{corr} = -An^\gamma$ of the correlation energy on the density and to estimate exponent $\gamma$. Calculations show that this method is limited to the values for a 3D (layered or multivalley) and 2D cases, $1/4 < \gamma < 1/3$. The exception is the case of single-valley TMDs, for which the power law for the correlation energy is inapplicable because of the absence of a small parameter.

We have analyzed the dependence of the exciton binding energy in monolayer heterostructures based on TMDs on their parameters and observed good agreement between the calculated and experimental values.

We have studied the metal–insulator transition. As the criterion for such a transition, we used the vanishing of the exciton binding energy upon an increase in the charge carrier density. Corresponding density $n_{dm}$ weakly depends on the number of valleys and the ratio of electron and hole masses.

The metal–insulator transition usually occurs in the gas phase. We have shown that the dielectric surroundings of the TMD monolayer can determine the phase (gaseous or liquid) in which the transition from the insulator to metal phase occurs. An example of such a behavior show heterostructures based on the
MoS₂ monolayer. If the monolayer is on the SiO₂ substrate, the metal–insulator transition occurs in the gas phase, while for a monolayer encapsulated in hBN, the transition apparently occurs in the liquid phase. It should be noted that the metal–insulator transition point in the encapsulated monolayer is very close to the critical point of the gas–liquid transition; therefore, the results obtained here are not very reliable and require refinement.

In our opinion, heterostructures based on the MoS₂ monolayer freely suspended or resting on the SiO₂ substrate are most interesting for investigation of EHL and the metal–insulator transition since these structures are characterized by the highest values of \( E_{\text{EHL}} \) and \( n_{\text{EHL}} \).

It would be interesting to find out how the dielectric surroundings and electron doping affect the metal–insulator transition and in which phase (gaseous or liquid) it occurs.

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